

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
28 April 2005 (28.04.2005)

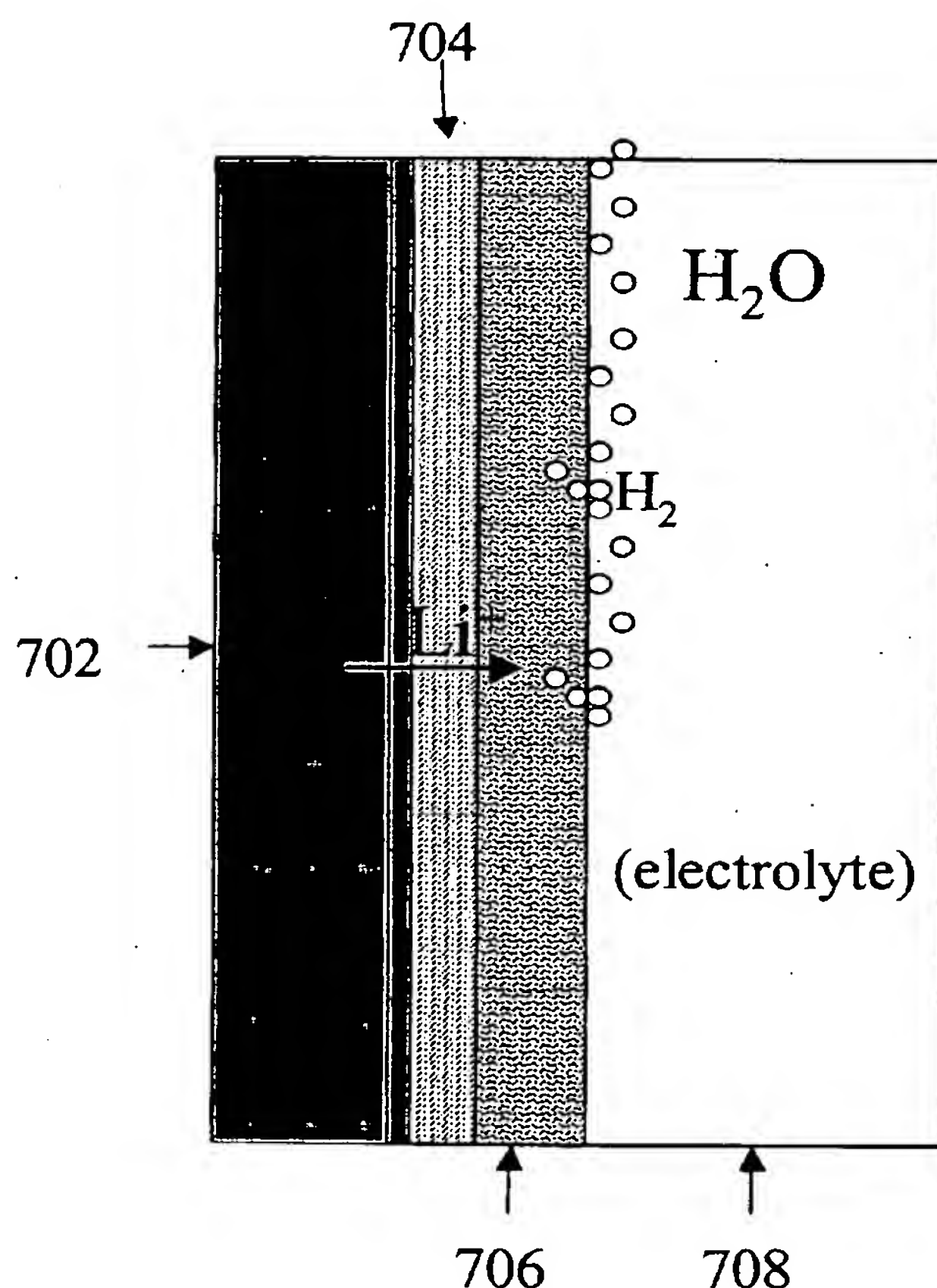
PCT

(10) International Publication Number
WO 2005/038953 A2

- (51) International Patent Classification⁷: **H01M**
- (21) International Application Number:
PCT/US2004/033424
- (22) International Filing Date: 8 October 2004 (08.10.2004)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
- | | | |
|------------|-------------------------------|----|
| 60/511,710 | 14 October 2003 (14.10.2003) | US |
| 60/518,948 | 10 November 2003 (10.11.2003) | US |
| 60/526,662 | 2 December 2003 (02.12.2003) | US |
| 60/527,098 | 3 December 2003 (03.12.2003) | US |
| 60/536,689 | 14 January 2004 (14.01.2004) | US |
| 60/536,688 | 14 January 2004 (14.01.2004) | US |
| 10/772,157 | 3 February 2004 (03.02.2004) | US |
- (71) Applicant (for all designated States except US): **POLY-PLUS BATTERY COMPANY** [US/US]; 2431 Fifth Street, Suite B, Berkeley, California 94710 (US).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **VISCO, Steven, J.** [US/US]; 546 Arlington Avenue, Berkeley, California 94707 (US). **NIMON, Yevgeniy, S.** [US/US]; 10 Cross Bridge Place, Danville, California 94526 (US).
- (74) Agent: **AUSTIN, James, E.**; Beyer Weaver & Thomas, LLP, P.O. Box 70250, Oakland, CA 94612-0250 (US).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG,

[Continued on next page]

(54) Title: **ACTIVE METAL/AQUEOUS ELECTROCHEMICAL CELLS AND SYSTEMS**



(57) Abstract: Alkali (or other active) metal battery and other electrochemical cells incorporating active metal anodes together with aqueous cathode/electrolyte systems. The battery cells have a highly ionically conductive protective membrane adjacent to the alkali metal anode that effectively isolates (de-couples) the alkali metal electrode from solvent, electrolyte processing and/or cathode environments, and at the same time allows ion transport in and out of these environments. Isolation of the anode from other components of a battery cell or other electrochemical cell in this way allows the use of virtually any solvent, electrolyte and/or cathode material in conjunction with the anode. Also, optimization of electrolytes or cathode-side solvent systems may be done without impacting anode stability or performance. In particular, Li/water, Li/air and Li/metal hydride cells, components, configurations and fabrication techniques are provided.

WO 2005/038953 A2

ACTIVE METAL/AQUEOUS ELECTROCHEMICAL CELLS AND SYSTEMS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to active metal electrochemical devices. More particularly, this invention relates to active metal/aqueous (e.g., lithium) battery cells made possible by active metal electrode structures having ionically conductive membranes for protection of the active metal from deleterious reaction with air, moisture and other battery cell components, methods for their fabrication and applications for their use.

10 2. Description of Related Art

The low equivalent weight of alkali metals, such as lithium, render them particularly attractive as a battery electrode component. Lithium provides greater energy per volume than the traditional battery standards, nickel and cadmium. Unfortunately, no rechargeable lithium metal batteries have yet succeeded in the market place.

The failure of rechargeable lithium metal batteries is largely due to cell cycling problems. On repeated charge and discharge cycles, lithium "dendrites" gradually grow out from the lithium metal electrode, through the electrolyte, and ultimately contact the positive electrode. This causes an internal short circuit in the battery, rendering the battery unusable after a relatively few cycles. While cycling, lithium electrodes may also grow "mossy" deposits that can dislodge from the negative electrode and thereby reduce the battery's capacity.

To address lithium's poor cycling behavior in liquid electrolyte systems, some researchers have proposed coating the electrolyte facing side of the lithium negative electrode with a "protective layer." Such protective layer must conduct lithium ions, but at the same time prevent contact between the lithium electrode surface and the bulk electrolyte. Many techniques for applying protective layers have not succeeded.

Some contemplated lithium metal protective layers are formed *in situ* by reaction between lithium metal and compounds in the cell's electrolyte that contact the lithium. Most of these *in situ* films are grown by a controlled chemical reaction after the battery is assembled. Generally, such films have a porous morphology allowing some electrolyte to penetrate to the bare lithium metal surface. Thus, they fail to adequately protect the lithium electrode.

environments that are normally highly corrosive to Li or other active metals, and at the same time allows ion transport in and out of these potentially corrosive environments. The protective membrane is thus chemically compatible with active metal (e.g., lithium) on one side and a wide array of materials, including those that are normally highly corrosive to Li or other active metals on the other side, while at the same time allowing ion transport from one side to the other. In this way, a great degree of flexibility is permitted the other components of an electrochemical device, such as a battery cell, made with the protected active metal electrodes. Isolation of the anode from other components of a battery cell or other electrochemical cell in this way allows the use of virtually any solvent, electrolyte and/or cathode material in conjunction with the anode. Also, optimization of electrolytes or cathode-side solvent systems may be done without impacting anode stability or performance.

Such a protected active metal anode may be used with a wide array of solvents, electrolytes and cathode materials (including those more stable in lithium metal systems, such as are used in lithium-sulfur battery systems described in the patents of PolyPlus Battery Company, for example, US Patents 6,025,094, issued 02/15/00, 6,402,795, issued 06/11/02, 6,214,061, issued 04/10/01 and 6,413,284, issued 07/02/02, and US Patent Application No. 10/686,189, filed 10/14/03, each of which is incorporated by reference herein in its entirety for all purposes); and more Li-corrosive materials including air, ionic (including protic) solutions, aqueous electrolytes, molten salts, and ionic liquids, for example, operating conditions (including high through low temperatures) and discharge rate regimes (including high through low discharge rates). Li anode corrosion is not an issue and the electrolyte compatibility with the anode is not a concern. A few examples of desirable battery cells in accordance with the present invention include Li-air; Li-aqueous electrolyte; and Li-sea/salt water. Other novel and useful electrochemical devices are also rendered possible in accordance with the present invention, as described further below. The use of cathode materials extremely reactive with Li is also possible by using protective composites in accordance with the present invention, for example PbSnF₄ and the like, for Li/F batteries.

The present invention uses ionically conductive membranes for decoupling the active metal anode and cathode sides of an active metal electrochemical cell. The membranes may be incorporated in active metal negative electrode (anode) structures

lithium electrode shows no evidence of corrosion/chemical reaction with aqueous electrolytes, and results in batteries that should have wide commercial appeal.

In various aspects, the invention relates to an active metal/aqueous battery cell. The battery cell includes an active metal anode having a first surface and a second surface; a cathode structure with an electronically conductive component, an ionically conductive component, and an electrochemically active component. At least one cathode structure component comprises an aqueous constituent. An ionically conductive protective membrane is disposed on the first surface of the anode, the membrane having one or more materials configured to provide a first surface chemically compatible with the active metal of the anode in contact with the anode, and a second surface substantially impervious to and chemically compatible with the cathode structure and in contact with the cathode structure.

Exemplary cells in accordance with the present invention include Li/water, Li/air and Li/metal hydride batter cells and other electrochemical cells.

The invention also provides a variety of cell and component fabrication techniques, cell components and configurations.

These and other features of the invention are further described and exemplified in the detailed description below.

BRIEF DESCRIPTION OF THE DRAWINGS

5 Fig. 1 is a schematic illustration of an active metal battery cell incorporating an ionically conductive protective membrane in accordance with the present invention.

Figs. 2A and B are a schematic illustrations of ionically conductive protective membrane battery separators in accordance with the present invention.

10 Fig. 3A is a schematic illustration of an active metal anode structure incorporating an ionically conductive protective laminate composite membrane in accordance with the present invention.

Fig. 3B is a schematic illustration of an active metal anode structure incorporating an ionically conductive protective graded composite membrane in accordance with the present invention.

15 Figs. 4A-B, 5 and 6A-B are schematic illustrations of alternative methods of making an electrochemical device structure incorporating an ionically conductive protective membrane in accordance with the present invention.

invention as defined by the appended claims. In the following description, numerous specific details are set forth in order to provide a thorough understanding of the present invention. The present invention may be practiced without some or all of these specific details. In other instances, well known process operations have not
5 been described in detail in order not to unnecessarily obscure the present invention.

When used in combination with "comprising," "a method comprising," "a device comprising" or similar language in this specification and the appended claims, the singular forms "a," "an," and "the" include plural reference unless the context clearly dictates otherwise. Unless defined otherwise, all technical and scientific terms
10 used herein have the same meaning as commonly understood to one of ordinary skill in the art to which this invention belongs.

Introduction

The present invention concerns alkali (or other active) metal battery cells and electrochemical cells incorporating them together with aqueous cathode/electrolyte
15 systems. The battery cell negative electrode (anode) has a highly ionically conductive (at least about 10^{-7} S/cm, and more preferably at least 10^{-6} S/cm, for example 10^{-5} S/cm to 10^{-4} S/cm, and as high as 10^{-3} S/cm or higher) protective membrane adjacent to the alkali metal anode that effectively isolates (de-couples) the alkali metal electrode from solvent, electrolyte processing and/or cathode environments, including such
20 environments that are normally highly corrosive to Li or other active metals, and at the same time allows ion transport in and out of these potentially corrosive environments. The protective membrane is thus chemically compatible with active metal (e.g., lithium) on one side and a wide array of materials, including those including those that are normally highly corrosive to Li or other active metals on the other side, while at
25 the same time allowing ion transport from one side to the other. In this way, a great degree of flexibility is permitted the other components of an electrochemical device, such as a battery cell, made with the protected active metal electrodes. Isolation of the anode from other components of a battery cell or other electrochemical cell in this way allows the use of virtually any solvent, electrolyte and/or cathode material in
30 conjunction with the anode. Also, optimization of electrolytes or cathode-side solvent systems may be done without impacting anode stability or performance.

Such a protected active metal anode may be used with a wide array of solvents, electrolytes and cathode materials (including those more stable in lithium metal

The membrane may have any suitable composition, for example, it may be a monolithic material chemically compatible with both the anode and cathode environments, or a composite composed of at least two components of different materials having different chemical compatibilities, one chemically compatible with
5 the anode environment and the other chemically compatible with the cathode environment.

Composite membranes may be composed of at least two components of different materials having different chemical compatibility requirements. The composite may be composed of a laminate of discrete layers of materials having
10 different chemical compatibility requirements, or it may be composed of a gradual transition between layers of the materials. By "chemical compatibility" (or "chemically compatible") it is meant that the referenced material does not react to form a product that is deleterious to battery cell operation when contacted with one or more other referenced battery cell components or manufacturing, handling or storage
15 conditions.

A first material layer of the composite is both ionically conductive and chemically compatible with an active metal electrode material. Chemical compatibility in this aspect of the invention refers to a material that is chemically stable and therefore substantially unreactive when contacted with an active metal
20 electrode material. Active metals are highly reactive in ambient conditions and can benefit from a barrier layer when used as electrodes. They are generally alkali metals such (e.g., lithium, sodium or potassium), alkaline earth metals (e.g., calcium or magnesium), and/or certain transitional metals (e.g., zinc), and/or alloys of two or more of these. The following active metals may be used: alkali metals (e.g., Li, Na,
25 K), alkaline earth metals (e.g., Ca, Mg, Ba), or binary or ternary alkali metal alloys with Ca, Mg, Sn, Ag, Zn, Bi, Al, Cd, Ga, In. Preferred alloys include lithium aluminum alloys, lithium silicon alloys, lithium tin alloys, lithium silver alloys, and sodium lead alloys (e.g., Na₄Pb). A preferred active metal electrode is composed of lithium. Chemical compatibility also refers to a material that may be chemically
30 stable with oxidizing materials and reactive when contacted with an active metal electrode material to produce a product that is chemically stable against the active metal electrode material and has the desirable ionic conductivity (i.e., a first layer material). Such a reactive material is sometimes referred to as a "precursor" material.

Fig. 1 is a conceptual illustration of an ionically conductive protective membrane in accordance with the present invention in context as it would be used in an active metal/aqueous battery cell 120, such as a lithium/water, lithium/air or lithium/metal hydride battery cell, in accordance with the present invention. The membrane 100 is both ionically conductive and chemically compatible with an active metal (e.g., lithium) electrode (anode) 106 on one side, and substantially impervious, ionically conductive and chemically compatible with a cathode structure 110 having an electronically conductive component, an ionically conductive component, and an electrochemically active component, with at least one cathode structure component being or including an aqueous constituent. The ionic conductivity of the membrane is at least 10^{-7} S/cm, generally at least 10^{-6} S/cm, for example at least 10^{-5} S/cm to 10^{-4} S/cm, and as high as 10^{-3} S/cm or higher. The active metal anode 106 in contact with the first side of the protective membrane is connected with a current collector 108 composed of a conductive metal, such as copper, that is generally inert to and does not alloy with the active metal. The electronically conductive component, for example in Li/water and Li/air cells, a porous catalytic electronically conductive support, not shown in this conceptual depiction, is generally provided adjacent to the protective membrane on the cathode, provides electron transport from the anode (via a cathode current collector 112) and facilitates electroreduction of the cathode active material.

The protective membrane may be a composite composed of two or more materials that present sides having different chemical compatibility to the anode and electrolyte and/or cathode, respectively. The composite is composed of a first layer of a material that is both ionically conductive and chemically compatible with an active metal electrode material. The composite also includes second layer of a material that is substantially impervious, ionically conductive and chemically compatible with the first material and the cathode/electrolyte environment.

As described further below, given the protection afforded by the protective membranes of the present invention, the electrolytes and/or cathodes combined with the protected anodes of the present invention may include a wide variety of materials including, but not limited to, those described in the patents of PolyPlus Battery Company, referenced herein below.

Fig. 2A illustrates a protective membrane composite battery separator in accordance with one embodiment of the present invention. The separator 200

first material or precursor and environments normally corrosive to the active metal of the anode, including glassy or amorphous metal ion conductors, such as a phosphorus-based glass, oxide-based glass, phosphorus-oxynitride-based glass, sulfur-based glass, oxide/sulfide based glass, selenide based glass, gallium based glass, germanium-based glass or boracite glass (such as are described D.P. Button et al., Solid State Ionics, Vols. 9-10, Part 1, 585-592 (December 1983); ceramic active metal ion conductors, such as lithium beta-alumina, sodium beta-alumina, Li superionic conductor (LISICON), Na superionic conductor (NASICON), and the like; or glass-ceramic active metal ion conductors. Specific examples include LiPON, $\text{Li}_3\text{PO}_4\cdot\text{Li}_2\text{S}\cdot\text{SiS}_2$, $\text{Li}_2\text{S}\cdot\text{GeS}_2\cdot\text{Ga}_2\text{S}_3$, $\text{Li}_2\text{O}\cdot 11\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O}\cdot 11\text{Al}_2\text{O}_3$, $(\text{Na}, \text{Li})_{1+x}\text{Ti}_{2-x}\text{Al}_x(\text{PO}_4)_3$ ($0.6 \leq x \leq 0.9$) and crystallographically related structures, $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$, $\text{Li}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$, $\text{Na}_5\text{ZrP}_3\text{O}_{12}$, $\text{Na}_5\text{TiP}_3\text{O}_{12}$, $\text{Na}_3\text{Fe}_2\text{P}_3\text{O}_{12}$, $\text{Na}_4\text{NbP}_3\text{O}_{12}$, $\text{Li}_5\text{ZrP}_3\text{O}_{12}$, $\text{Li}_5\text{TiP}_3\text{O}_{12}$, $\text{Li}_3\text{Fe}_2\text{P}_3\text{O}_{12}$ and $\text{Li}_4\text{NbP}_3\text{O}_{12}$, and combinations thereof, optionally sintered or melted. Suitable ceramic ion active metal ion conductors are described, for example, in US Patent No. 4,985,317 to Adachi *et al.*, incorporated by reference herein in its entirety and for all purposes.

A particularly suitable glass-ceramic material for the second layer of the protective composite is a lithium ion conductive glass-ceramic having the following composition:

Composition	mol %
P_2O_5	26-55%
SiO_2	0-15%
$\text{GeO}_2 + \text{TiO}_2$	25-50%
in which GeO_2	0--50%
TiO_2	0--50%
ZrO_2	0-10%
M_2O_3	$0 < 10\%$
Al_2O_3	0-15%
Ga_2O_3	0-15%
Li_2O	3-25%

Docket No. PLUSP027), filed October 14, 2003, and titled IONICALLY CONDUCTIVE COMPOSITES FOR PROTECTION OF ACTIVE METAL ANODES, and US Patent application No. 10/731,771 (Attorney Docket No. PLUSP027X1), filed December 5, 2003, and titled IONICALLY CONDUCTIVE COMPOSITES FOR PROTECTION OF ACTIVE METAL ANODES. These applications are incorporated by reference herein in their entirety for all purposes.

The composite barrier layer should have an inherently high ionic conductivity. In general, the ionic conductivity of the composite is at least 10^{-7} S/cm, generally at least about 10^{-6} to 10^{-5} S/cm, and may be as high as 10^{-4} to 10^{-3} S/cm or higher. The thickness of the first precursor material layer should be enough to prevent contact between the second material layer and adjacent materials or layers, in particular, the active metal of the anode with which the separator is to be used. For example, the first material layer may have a thickness of about 0.1 to 5 microns; 0.2 to 1 micron; or about 0.25 micron.

The thickness of the second material layer is preferably about 0.1 to 1000 microns, or, where the ionic conductivity of the second material layer is about 10^{-7} S/cm, about 0.25 to 1 micron, or, where the ionic conductivity of the second material layer is between about 10^{-4} about 10^{-3} S/cm, about 10 to 1000 microns, preferably between 1 and 500 microns, and more preferably between 10 and 100 microns, for example 20 microns.

When the first material layer is a precursor material chemically stable in air, for example Cu_3N or LiPON, the protective composite battery separator may be handled or stored in normal ambient atmospheric conditions without degradation prior to incorporation into a battery cell. When the separator is incorporated into a battery cell, the precursor layer 202 is contacted with an active metal (e.g., lithium) electrode. The precursor reacts with the active metal to form an ionically conductive material that is chemically compatible with the active metal electrode material. The second layer is contacted with an electrolyte to which a cathode and current collector is or has been applied. Alternatively, the second layer acts as the sole electrolyte in the battery cell. In either case, the combination of the two layers in the protective composite protects the active metal electrode and the electrolyte and/or cathode from deleterious reaction with one another.

include Li_3N , Li_3P , LiI , LiBr , LiCl and LiF . The thickness of the first material layer is preferably about 0.1 to 5 microns, or 0.2 to 1 micron, for example about 0.25 micron.

Active metal electrode materials (e.g., lithium) may be applied to these materials, or they may be formed *in situ* by contacting precursors such as metal
 5 nitrides, metal phosphides, metal halides, red phosphorus, iodine and the like with lithium. The *in situ* formation of the first layer may be by way of conversion of the precursors to a lithiated analog, for example, according to reactions of the following type (using P, Cu_3N , and PbI_2 precursors as examples):

1. $3\text{Li} + \text{P} = \text{Li}_3\text{P}$ (reaction of the precursor to form Li-ion conductor);

10 2(a). $3\text{Li} + \text{Cu}_3\text{N} = \text{Li}_3\text{N} + 3\text{Cu}$ (reaction to form Li-ion conductor/metal composite);

2(b). $2\text{Li} + \text{PbI}_2 = 2\text{LiI} + \text{Pb}$ (reaction to form Li-ion conductor/metal composite).

First layer composites, which may include electronically conductive metal
 15 particles, formed as a result of *in situ* conversions meet the requirements of a first layer material for a protective composite in accordance with the present invention and are therefore within the scope of the invention.

A second layer 306 of the protective composite is composed of a substantially impervious, ionically conductive and chemically compatible with the first material or
 20 precursor, including glassy or amorphous metal ion conductors, such as a phosphorus-based glass, oxide-based glass, phosphorus-oxynitride-based glass, sulfur-based glass, oxide/sulfide based glass, selenide based glass, gallium based glass, germanium-based glass or boracite glass; ceramic active metal ion conductors, such as lithium beta-alumina, sodium beta-alumina, Li superionic conductor (LISICON), Na superionic
 25 conductor (NASICON), and the like; or glass-ceramic active metal ion conductors. Specific examples include LiPON , $\text{Li}_3\text{PO}_4 \cdot \text{Li}_2\text{S} \cdot \text{SiS}_2$, $\text{Li}_2\text{S} \cdot \text{GeS}_2 \cdot \text{Ga}_2\text{S}_3$, $\text{Li}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$, $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$, $(\text{Na}, \text{Li})_{1+x}\text{Ti}_{2-x}\text{Al}_x(\text{PO}_4)_3$ ($0.6 \leq x \leq 0.9$) and crystallographically related structures, $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$, $\text{Li}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$, $\text{Na}_5\text{ZrP}_3\text{O}_{12}$, $\text{Na}_5\text{TiP}_3\text{O}_{12}$, $\text{Na}_3\text{Fe}_2\text{P}_3\text{O}_{12}$, $\text{Na}_4\text{NbP}_3\text{O}_{12}$, $\text{Li}_5\text{ZrP}_3\text{O}_{12}$, $\text{Li}_5\text{TiP}_3\text{O}_{12}$, $\text{Li}_3\text{Fe}_2\text{P}_3\text{O}_{12}$ and $\text{Li}_4\text{NbP}_3\text{O}_{12}$, and
 30 combinations thereof, optionally sintered or melted. Suitable ceramic ion active metal ion conductors are described, for example, in US Patent No. 4,985,317 to Adachi *et al.*, incorporated by reference herein in its entirety and for all purposes. Suitable glass-ceramic ion active metal ion conductors are described, for example, in US

many, but not all, embodiments the second material will dominate. For example, suitable ratios of first to second materials may be 1-1000 or 1-500, for example about 1 to 200 where the second material has greater strength and ionic conductivity than the first (e.g., 2000Å of LiPON and 20-30microns of a glass-ceramic such as described
5 herein). The transition between materials may occur over any (e.g., relatively short, long or intermediate) distance in the composite.

Also, an approach may be used where a first material and second material are coated with another material such as a transient and/or wetting layer. For example, a glass-ceramic plate such as described herein (e.g. from OHARA Corp.) is coated with
10 a LiPON layer, followed by a thin silver (Ag) coating. When lithium is evaporated onto this structure, the Ag is converted to Ag-Li and diffuses, at least in part, into the greater mass of deposited lithium, and a protected lithium electrode is created. The thin Ag coating prevents the hot (vapor phase) lithium from contacting and adversely reaction with the LiPON first material layer. After deposition, the solid phase lithium
15 is stable against the LiPON. A multitude of such transient/wetting (e.g., Sn) and first layer material combinations can be used to achieve the desired result.

A protective membrane in accordance with the present invention may be formed using a variety of methods. These include deposition or evaporation. Protective membrane composites of the present invention may be formed by
20 deposition or evaporation (including e-beam evaporation) of the first layer of material or precursor on the second layer of material. Also, as noted above and described further below, the first layer may be formed *in situ* from the non-deleterious reaction of one or more precursors with an active metal electrode or material, by deposition or evaporation of lithium on the precursor, by direct contact of the precursor with a
25 lithium metal (e.g., foil), or by plating of the precursor with lithium through a second layer material. In some embodiments, the second layer material may also be formed on the first layer material, as described further below.

Referring to Fig. 4A, a first method for forming a protective membrane composite in accordance with the present invention is shown. A first layer, that is a
30 highly ionically conductive active metal chemically compatible material, is directly deposited onto a second layer material, that is a substantially impervious, ionically conductive material, for example, a highly ionically conductive glass or glass-ceramic material such as LiPON or a glass-ceramic material described above. This can be

material, and the other for the deposition of a second component material, such as an glass-ceramic, for example as available for OHARA Corp., may be used. The first plasma spray process begins laying down a layer of pure glass-ceramic material, followed by a gradual decrease in flow as the second plasma spray torch is gradually
5 turned on, such that there is a gradient from pure glass-ceramic to a continuous transition from glass-ceramic to pure LiPON or Li_3N , etc. In this way, one side of the membrane is stable to active metal (e.g., lithium, sodium, etc.) and the other side is substantially impervious and stable to the cathode, other battery cell components and preferably to ambient conditions. Electron beam deposition or thermal spray
10 deposition may also be used. Given the parameters described herein, one or skill in the art will be able to use any of these techniques to form the graded composites of the invention.

To form a protected anode, lithium is then bonded to the graded membrane on the first layer material (stable to active metal) side of the graded protective composite,
15 for example by evaporation of lithium onto the protective composite as described above. It may also be desirable to add a bonding layer on top of the lithium stable side of the graded composite protective layer, such as Sn, Ag, Al, etc., before applying lithium.

In any of the forgoing methods described with reference to Figs. 4A-B and 5,
20 rather than forming a lithium (or other active metal) layer on the first layer material or precursor, the first layer material or precursor of the protective composite may be contacted with the lithium by bonding metallic lithium to the protective interlayer material or precursor, for example by direct contact with extruded lithium metal foil.

In a further embodiment, a suitable substrate, e.g., having a wetting layer, such
25 as a film of tin on copper, may be coated with a first layer material precursor, e.g., Cu_3N . This may then be coated with a second layer material, e.g., a (ionically) conductive glass. An active metal electrode may then be formed by plating the tin electrode with lithium (or other active metal), through the first and second layer materials. The Cu_3N precursor is also converted to Li_3N by this operation to complete
30 the protective composite in accordance with the present invention on a lithium metal electrode. Details of an active metal plating process are described in commonly assigned US Patent No. 6,402,795, previously incorporated by reference.

According to this method, a thin layer of polymer may be applied to the second material layer (e.g., conductive glass) using brushing, dipping, or spraying. For example, a conductive glass layer may be coated with a thin (e.g, 0.5 to 2.0 micron, preferably 0.1 to 0.5 micron) layer of P2VP in this way.

5 One technique for applying an iodine coating is sublimation of crystalline iodine that can be achieved at room temperature (e.g., about 20 to 25°C) in a reactor placed in the dry box or in a dry room. A sublimed layer of iodine can be made very thin (e.g., 0.05 to 1.0 microns and the rate of sublimation can be adjusted by varying the temperature or distance between the substrate and source of iodine.

10 Alternatively, high concentrations (e.g., 50 to 100 g/liter of iodine can be dissolved in an organic solvent, such as acetonitrile and n-heptane. Dissolved iodine can be coated on the conductive glass surface by such methods as dip coating, spraying or brushing, among others. In this case, treatment conditions can be easily changed by varying the length of coating treatment and iodine concentrations.
15 Examples of iodine sources for this technique include metal iodides are AgI and PbI₂, which are known to be used as the cathode materials in solid-state batteries with Li anode and LiI-based solid electrolyte.

Then, lithium (or other active metal) is contacted with the polymer-iodine complex on the conductive glass (or other second layer material), for example by
20 evaporation or pressing onto the glass coated with this complex. The result is a LiI-containing composite protective barrier layer on the Li anode.

Referring to Fig. 6B, an alternative embodiment of this aspect of the present invention is shown. A conductive glass (or other second layer material) surface is coated with a thin layer of iodine, such as by a technique described above, that can
25 react with Li forming LiI layer (A).

Active metal, for example lithium foil, can be coated with a thin layer of polymer (B), for example as described above, and then contacted with the iodine layer on the glass. After assembly, iodine reacts with the polymer layer and, as a result, LiI-containing composite protective barrier layer with reduced impedance is formed.

30 The protected anode structures with fully-formed protective layers and battery separators incorporating ambient stable precursors described above may be handled or stored in normal ambient atmospheric conditions without degradation prior to incorporation into a battery cell.

embodiments below, the cells have an electronically conductive support structure electrically connected with the anode to allow electron transfer to reduce the cathode material (e.g., H_2O in a Li/water cell). The electronically conductive support structure is generally porous to allow fluid flow and either catalytic (e.g., Ni, Pt) or treated with a catalyst to catalyze the reduction of the cathode material. An aqueous electrolyte with suitable ionic conductivity is generally in contact with the electronically conductive support structure to allow ion transport through the electronically conductive support structure to complete the redox reaction.

The electronically conductive support structure may also be treated with an ionomer, such as per-fluoro-sulfonic acid polymer film (e.g., du Pont NAFION) to expand the range of acceptable aqueous electrochemically active components to those having little or no native ionic conductivity. An additional advantage of ionomers like NAFION is that the salt is chemically bonded to the polymer backbone, and therefore cannot be flushed out in flow-through or open cell implementations, described below.

The battery cells may be primary or secondary cells. For primary cells, the cathode side of the cells may be open to the environment and the oxidized lithium on the cathode side of the cell may simply disperse into the environment. Such a cell may be referred to as an "open" cell. Cells for marine applications which use sea water as an electrochemically active and ionically conductive material are an example. For secondary cells, the oxidized lithium is retained in a reservoir on the cathode side of the cell to be available to recharge the anode by moving the Li ions back across the protective membrane when the appropriate potential is applied to the cell. Such a cell may be referred to as a "closed" cell. Such closed cells require venting for the hydrogen produced at the cathode. Appropriate battery cell vents are known in the art.

An example of an active metal/water battery cell in accordance with the present invention is a lithium/water battery cell, as conceptually illustrated above in Fig. 1. Fig. 7 illustrates a specific implementation of such a lithium/water battery cell in accordance with the present invention. The battery cell 700 includes a lithium negative electrode (anode) 702. Alternatively, another active metal, particularly an alkali metal, may be used. The lithium metal electrode can be bonded to a lithium ion conductive protective membrane 704 according to any of the techniques described herein and in the patent applications incorporated by reference, as described above, with or without the use of a bond coat such as a thin layer of Ag or other suitable

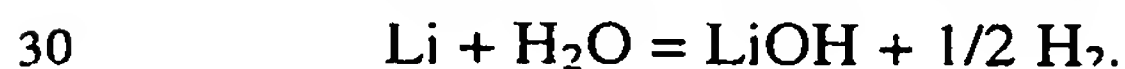
conceptually separate elements of the battery cell. Suitable electrolytes for the Li/water battery cell of the invention include any aqueous electrolyte with suitable ionic conductivity. Suitable electrolytes may be acidic, for example, strong acids like HCl, H₂SO₄, H₃PO₄ or weak acids like acetic acid/Li acetate; basic, for example, 5 LiOH; neutral, for example, sea water, LiCl, LiBr, LiI; or amphoteric, for example, NH₄Cl, NH₄Br, etc

The suitability of sea water as an electrolyte enables a battery cell for marine applications with very high energy density. Prior to use, the cell structure is composed of the protected anode and the porous electronically conductive support 10 structure (electronically conductive component). When needed, the cell is completed by immersing it in sea water which provides the electrochemically active and ionically conductive components. Since the latter components are provided by the sea water in the environment, they need not be transported as part of the battery cell prior to its use (and thus need not be included in the cell's energy density calculation). Such a cell is 15 referred to as an "open" cell since the reaction products on the cathode side are not contained. Such a cell is, therefore, a primary cell.

Secondary Li/water cells are also possible in accordance with the invention. As noted above, such cells are referred to as "closed" cells since the reaction products on the cathode side are contained on the cathode side of the cell to be available to 20 recharge the anode by moving the Li ions back across the protective membrane when the appropriate recharging potential is applied to the cell.

As noted above and described further below, in another embodiment of the invention, ionomers coated on the porous catalytic electronically conductive support reduce or eliminate the need for ionic conductivity in the electrochemically active 25 material.

The electrochemical reaction that occurs in a Li/water cell is a redox reaction in which the electrochemically active cathode material gets reduced. In a Li/water cell, the catalytic electronically conductive support facilitates the redox reaction. As noted above, while not so limited, in a Li/water cell, the cell reaction is believed to be:



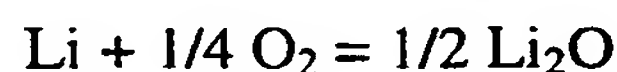
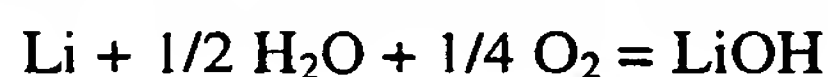
The half-cell reactions at the anode and cathode are believed to be:



density cells for marine applications having a protected Li anode in accordance with the present invention can utilize hydrogen peroxide dissolved in sea water and continuously flowing through the cell.

Active Metal/Air Battery Cells

5 Active metal/air battery cells are another class of active metal/aqueous cells in accordance with the present invention. These cells have an active metal, e.g., alkali metal, e.g., lithium (Li), anode with a protective membrane and a cathode structure with air as the electrochemically active component. While not so limited, the electrochemical reaction between the Li ions from the anode and the air is believed to
10 be described by one or more of the following reaction schemes:



Thus both moisture (H₂O) and oxygen in the air are participants in the electrochemical
15 reaction.

The anode side of these cells is the same as for any of the active metal/aqueous cells provided herein, and is described above. In a cell, any part of the active metal electrode that is not covered by the protective membrane will generally be sealed off from the air cathode environment, such as by a current collector material (e.g.,
20 copper), an o-ring seal, a crimp seal, polymer or epoxy sealant, or combination of these.

The cathode side of these cells includes a cathode structure with an electronically conductive component, an ionically conductive component, and air as an electrochemically active component. The air electrochemically active component
25 of these cells includes moisture to provide water for the electrochemical reaction. As described further with reference to specific embodiments below, the cells have an electronically conductive support structure electrically connected with the anode to allow electron transfer to reduce the air cathode active material. The electronically conductive support structure is generally porous to allow fluid (air) flow and either
30 catalytic or treated with a catalyst to catalyze the reduction of the cathode active material. An aqueous electrolyte with suitable ionic conductivity or ionomer is also in contact with the electronically conductive support structure to allow ion transport within the electronically conductive support structure to complete the redox reaction.

typical ionomeric electrolyte is composed of a hydrated (water) Li ion conductive polymer such as a per-fluoro-sulfonic acid polymer film (e.g., du Pont NAFION). The air diffusion membrane adjusts the air (oxygen) flow. The hydrophobic layer prevents penetration of the cell's electrolyte into the air-diffusion membrane. This layer
5 usually contains carbon and Teflon particles. The catalyst layer usually contains a high surface area carbon and a catalyst for acceleration of reduction of oxygen gas. Metal oxides, for example MnO_2 , are used as the catalysts for oxygen reduction in most of the commercial cathodes. Alternative catalysts include metal macrocycles such as cobalt phthalocyanine, and highly dispersed precious metals such as platinum
10 and platinum/ruthenium alloys. Since the air electrode structure is chemically isolated from the active metal electrode, the chemical composition of the air electrode is not constrained by potential reactivity with the anode active material. This can allow for the design of higher performance air electrodes using materials that would normally attack unprotected metal electrodes.

15 Since metal/air batteries obtain the cathode active reactant from the ambient environment, the volumetric and gravimetric energy densities are very high. The high energy density of metal/air batteries makes them attractive for a wide variety of applications where weight and size are a premium. Unfortunately, conventional metal/air batteries suffer from parasitic reactions in which the metal electrode
20 corrodes to generate hydrogen. The anode corrosion reaction can be minimized by incorporating KOH in the electrolyte. However, this introduces another problem as CO_2 from the air is converted to K_2CO_3 in the air electrode, thereby forming precipitates that cause premature failure of the cell. Such problems are eliminated by the subject invention in that the active metal electrode is isolated from the aqueous
25 electrolyte, preventing corrosion of the anode. Since the anode does not corrode in the electrolyte solution, and is in fact de-coupled from it, the air electrode can be formulated with neutral (LiCl), basic (KOH), or acidic (NH_4Cl , HCl , etc.) electrolyte. While not so limited, for the case of acidic electrolyte, shown below, the cell reaction is believed to proceed by forming lithium chloride. In such a cell, the air electrode
30 does not scavenge CO_2 from the air, and there is no K_2CO_3 formation.



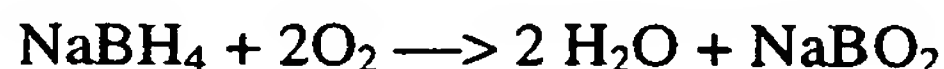
Metal hydride alloys are well known to those skilled in the art, and are generally chosen from rare earth based alloys (Misch metal) designated as AB₅ (LaNi₅ and LaCo₅ with partial substitutions to improve performance) and AB₂ alloys consisting of titanium and zirconium (such as ZrNi₂). The metal hydride electrode is typically engineered as a highly porous structure having a perforated nickel foil or grid onto which a polymer-bonded active hydrogen storage alloy is coated. The metal hydride electrode is used commercially in the nickel/metal hydride (Ni/MH) battery. In this chemistry, an alkaline electrolyte is used, and the hydride alloys are modified to perform well in alkaline conditions. For the case of a Li/MH battery, the electrolyte will be acidic, and so the composition of the AB₅ or AB₂ alloy may be modified to cycle well in acidic electrolytes.

Li/Water Battery and Hydrogen Generator for Fuel Cell

The use of protective layers on active metal electrodes in accordance with the present invention allows the construction of active metal/water batteries that have negligible corrosion currents, described above. The Li/water battery has a very high theoretical energy density of 8450 Wh/kg. The cell reaction is $\text{Li} + \text{H}_2\text{O} = \text{LiOH} + 1/2 \text{H}_2$. Although the hydrogen produced by the cell reaction is typically lost, in this embodiment of the present invention it is used to provide fuel for an ambient temperature fuel cell. The hydrogen produced can be either fed directly into the fuel cell or it can be used to recharge a metal hydride alloy for later use in a fuel cell. At least one company, Millenium Cell <<<http://www.millenniumcell.com/news/tech.html>>> makes use of the reaction of sodium borohydride with water to produce hydrogen. However, this reaction requires the use of a catalyst, and the energy produced from the chemical reaction of NaBH₄ and water is lost as heat.



When combined with the fuel cell reaction, $\text{H}_2 + \text{O}_2 = \text{H}_2\text{O}$, the full cell reaction is believed to be:



The energy density for this system can be calculated from the equivalent weight of the NaBH₄ reactant ($38/4 = 9.5$ grams/equiv.). The gravimetric capacity of NaBH₄ is 2820 mAh/g; since the voltage of the cell is about 1, the specific energy of this system

glass, ceramics, glass-ceramics and water-stable polymers. The insulating support is metallized in order to carry current. Insulating supports can be metallized by a process known as electroless deposition in which a catalyst and reducing agent are adsorbed onto the surface of the insulator before exposing it to a solution of metal ions in solution which are reduced to metal on the surface according to techniques known in the art. Typical metal coatings are copper and nickel. Nickel is particularly preferred for its catalytic properties (particularly in Li/water cells).

Suitable glass, ceramic, and glass-ceramic supports can be an inert material, or made from an ionically conductive material such as are suitable for the protective membrane described herein. The porous support may be made through tape-casting or extrusion of a glass or ceramic or glass-ceramic powder/polymer binder/solvent mixture. Onto the porous support a second layer of finer glass or ceramic or glass-ceramic powder could be laid down by tape-casting or extrusion such that when the two-layer article is fired, the coarse support layer retains porosity while the thin-film densifies completely to become the a component of the protective membrane. Alternatively, the support layer could be pre-fired, and then a thin-film laid down by tape-casting or extrusion, and fired to full density.

A glass, ceramic or glass-ceramic component of the protective membrane can also be applied by melt-spray techniques, such as plasma-spray and vacuum plasma-spray, or other thermal spray techniques; such films may also need heat treatment as described as described in the publication Jie Fu, *J. Amer. Ceram. Soc.*, **80** [7] p. 1901-1903 (1997) and the patents of OHARA Corp., previously cited and incorporated by reference herein, to improve the ionic conductivity of the solid. In such processes, the membrane material may be supplied to a plasma torch nozzle as a powder, and sprayed out of the nozzle as fine molten droplets. The molten droplets hit the substrate and solidify. In this manner, a glass, ceramic or glass-ceramic film can be directly deposited onto dense or porous substrates to produce either a porous or dense film, depending on operating parameters.

Suitable polymeric supports include polyethylene, polypropylene, Kevlar, Nylon, etc. As an example, a thin glass-ceramic layer may be tape-cast and fired to full density. Then the polymeric support would be deposited onto the glass-ceramic film by tape-casting of a polymer/binder/solvent film, and allowed to dry.

CVD, or plasma-spray. Onto the lithium compatible layer, it may be desirable to deposit a thin Ag transient coating by vacuum evaporation, as described above. Finally, a lithium electrode is either evaporated onto the assembly (i.e. Li/Ag/LiPON/Ni), or mechanically bonded to the assembly by pressing.

5 The cell will be completed when needed by the subsequent addition of water and electrolyte to the porous electronically conductive support, for example by immersing it in seawater or other aqueous electrolytic solution. In the actual battery cell, the lithium metal electrode will be isolated from the seawater environment by means of a hermetic seal that may be composed of elastomeric or epoxy resins.

10 The catalytic electronically conductive support may also be treated with an ionomer, such as per-fluoro-sulfonic acid polymer film (e.g., du Pont NAFION) to expand the range of acceptable electrolytes to those having little or no native ionic conductivity.

 The porous catalytic electronically conductive support may also be structurally
15 reinforced with a metal frame to enhance its rigidity and strength. The frame may be composed of any suitable metal, such as stainless steel or aluminum. In a particular embodiment, the frame may be arranged in a grid pattern, such as that illustrated below in Figs. 12. B and D.

Supported Protective Membrane Structure and Fabrication

20 The use of thin protective membranes is desirable for several reasons including reducing materials costs, reducing weight and therefore increasing energy density and facilitating ion transport through the membrane. In order to use the thinnest possible protective membrane layer for a Li/aqueous cell, a thin ionically conductive glass-ceramic (for example) film is produced by an appropriate technique, such as tape-casting. Film thicknesses of a few microns to many microns are well known to those
25 skilled in the art of tape-casting, and such films are routinely used in multi-layer ceramic capacitors. The ionically conducting glass-ceramic is tape-cast and then fired to full density. The 10 to 50 micron film is still fragile at this point.

 In another embodiment, the thin glass or glass-ceramic membrane could be
30 made by "draw-down" techniques as described by Sony Corporation and Shott Glass (T. Kessler, H. Wegener, T. Togawa, M. Hayashi, and T. Kakizaki, "Large Microsheet Glass for 40-in. Class PALC Displays," 1997, FMC2-3, downloaded from Shott Glass website; <http://www.schott.com/english>, incorporated herein by reference. In essence,

Elastomeric Seals

Fig. 13 shows an embodiment in accordance with the present invention in which a plurality of glass, ceramic or glass-ceramic ionically conductive protective plates are bonded into an array by elastomeric seals. In this manner the array has some conformability due to the elastomeric nature of the plate-to-plate seals. The plates may already be bonded to a porous catalytic electronically conductive substrate, and then lithium (or other active metal) could be deposited on the other side of the plates to form an anode and complete the solid state portion of the cell (the cathode/electrolyte being in the liquid state). Alternatively, complete solid state portions of cells could also be bonded together as shown in Fig. 13.

Tubular Construction

Fig. 14 shows a tubular construction embodiment of a Li/water or Li/air cell in accordance with the present invention. For example a porous nickel tube could be used as a support. An ionically conductive glass, ceramic or glass-ceramic film such as described herein could be deposited by a variety of techniques, on either the outside (A) or inside (B) of the tube. The tube could be closed or open ended. For example, an open ended tube may be used, and an ionically conductive glass-ceramic plasma-sprayed onto the outer surface, followed by the lithium compatible first component material (e.g., LiPON), a bond coat (e.g., Ag), and a lithium electrode, and finally a copper foil and end seals. The tube could be suspended in seawater, and used as a high energy density battery. Depending on whether the lithium is outside of the tube, or inside the tube as a central core, the seawater (or air in the case of a Li/air cell) will flow through the center of the tube or around the tube, respectively.

Capillary Construction

Fig. 15 shows a capillary construction embodiment of a Li/water or Li/air cell in accordance with the present invention. In this approach, thin diameter glass, ceramic or glass-ceramic capillaries are blown from a protective membrane material. The inner (or outer) surface is coated with by the lithium compatible first component material (e.g., LiPON(Ag)), and molten lithium is wicked into the capillary to form a high surface area protected anode fiber. Individual fibers are then coated with the porous catalytic electronically conductive support material. The high surface area to volume ratio for such fibers allows for high rate applications. A number of such fibers can be connected in parallel to create a high power lithium/water battery, and

outer layer (second composite layer) of a protective membrane against the aqueous environment of the electrolyte and cathode (water). These metal oxide Li conductors are stable in aqueous environments, but are unstable to lithium metal. In order to protect the OHARA membrane against metallic lithium, LiPON was used. The OHARA plates were in the range of 0.3 to 1 mm in thickness. The LiPON coating was in the range of 0.1 to 0.5 microns in thickness, and was deposited onto the OHARA plate by RF sputtering.

On top of the LiPON coating, a thin coating of Ag was formed by vacuum evaporation to prevent the reaction of hot evaporated lithium with the LiPON film. The Ag films were in the range of 200 to 1000 Å in thickness. LiPON can react with highly reactive Li from the vapor phase during Li vacuum deposition. Vacuum deposition of a thin film of Ag, Al, Sn or other Li alloy-forming metal onto the glass-ceramic surface can prevent the reaction LiPON surface with Li. The thickness of this metal film is from 50Å to 10000Å, preferably, from 100Å to 1000Å. In addition to protection of the first layer material against reaction with Li, a Li alloy-forming metal film can serve two more purposes. In some cases after formation the first layer material the vacuum needs to be broken in order to transfer this material through the ambient or dry room atmosphere to the other chamber for Li deposition. The metal film can protect the first layer against reaction with components of this atmosphere. In addition, the Li alloy-forming metal can serve as a bonding layer for reaction bonding of Li to the first layer material. When lithium is evaporated onto this structure, the Ag is converted to Ag-Li and diffuses, at least in part, into the greater mass of deposited lithium.

Following deposition of the Ag film, approximately 5 microns of lithium metal were evaporated onto the Ag film, creating a Li(Ag)/LiPON/OHARA protected lithium electrode. This protected lithium electrode is illustrated in Fig. 16. The protected electrode was fitted into an electrochemical cell by use of an o-ring such that the OHARA plate was exposed to an aqueous environment. In one case, the aqueous environment comprised a 0.5 M HCl + 1.0 M LiCl electrolyte. A platinum counter electrode was used to facilitate hydrogen reduction when the battery circuit was completed. An Ag/AgCl reference electrode was used to control potentials of the Li anode and Pt cathode in the cell. Measured values were recalculated into potentials in the Standard Hydrogen Electrode (SHE) scale. An open circuit potential (OCP) of

discharge voltage. It should be emphasized that in all previous experiments using an unprotected Li anode in seawater utilization of Li was very poor and at low and moderate current densities similar to those used in this example such batteries could not be used at all due to the extremely high rate of Li corrosion in a seawater (over 19 A/cm²).

Example 3: Li/Seawater cell with large capacity anode.

A lithium/sea (salt) water cell with a Pt wire cathode and a large capacity Li(Ag)/LiPON/glass-ceramic (OHARA Corp.) protected anode was built. Following deposition of the Ag film onto the LiPON on the OHARA plate, 50 um thick Li foil from Cyprus Foote Mineral Co. was pressed onto the Ag film to fabricate a thick protected Li anode. A Carver hydraulic press located in a dry room was used for the pressing operation. The applied pressure was around 800 kg/cm², and duration of pressing was 10 minutes. The Li surface was polished with a Tyvec fabric just before pressing onto the Ag film. The Ag film reacted with the Li foil forming a strong reaction bond. The seawater electrolyte composition was the same as in the previous example.

Fig. 23 shows a discharge (potential-time) curve at a discharge rate of 0.3 mA/cm². The cell exhibited long discharge. Discharge capacity delivered to the cut-off voltage of 2.0 V corresponded to the Li thickness over 20 μm. This amount of Li could be moved through the Li anode/aqueous electrolyte interface without destruction of the protective layers.

Example 4: Cell with protected Li electrode in aqueous electrolyte containing hydrogen peroxide as a dissolved oxidant

A Lithium/Hydrogen Peroxide cell was built with the Li(Ag)/LiPON/OHARA plate protected anode similar to one used in the previous example. Electrolyte was 1M solution of phosphoric acid (H₃PO₄) in water with addition of 5% hydrogen peroxide (H₂O₂) by weight. The volume of the electrolyte in the cell was 500 ml. A gold cathode for hydrogen peroxide reduction was made by vacuum coating of both sides of a carbon fiber paper (35 um thick from Lydall Technical Papers, Rochester, NY) with an approximately 3um thick Au layer.

Fig. 24 shows a discharge (potential-time) curve for a discharge rate of 0.3 mA/cm². The open circuit potential value (OCP) for the cell was close to 4.0 V. The cell exhibited a flat discharge potential of approximately 3.6 V.

Following deposition of the Ag film, approximately 5 microns of lithium metal were evaporated onto the Ag film, creating a Li(Ag)/LiPON/OHARA protected anode. The protected anode was fitted into an electrochemical cell by use of an o-ring such that the OHARA plate was exposed to the aqueous electrolyte environment.

5 The electrolyte used in this Li/air cell with protected anode was 0.5 M NH_4Cl + 0.5 M LiCl . Zirconia cloth from Zircar Products, Inc. was put onto the OHARA plate and filled with the electrolyte. A volume of the electrolyte was approximately 0.2 ml. An air electrode made for commercial Zn/Air batteries was used as a cathode in this experimental Li/Air cell.

10 An open circuit potential of 3.25 was observed for this cell. Fig. 25 shows discharge (potential-time) curve at discharge rate of 0.3 mA/cm^2 . The cell exhibited discharge voltage of approximately 3.1 V for about 1.0 hr (about 3.0 mAh/cm^2). This result shows that good performance can be achieved for Li/air cells with protected Li anode and an electrolyte that does not contain KOH, which is normally employed in
15 existing metal/Air batteries. KOH slows down corrosion of the metal (e.g., Zn), but draws CO_2 into the cell which causes damaging carbonization. As a result, conventional metal/air batteries have limited shelf-life. The Li/air cell described and tested herein is free from negative effect of electrolyte carbonization typical for existing metal/air batteries.

20 *Example 6: Li/Air cell with large capacity anode.*

A lithium/air cell was built with an air cathode similar to that used in Example 5, but with a Li(Ag)/LiPON/OHARA plate protected anode having much higher capacity. The electrolyte used in this Li/air cell with protected anode comprised 0.5 M LiOH . Following deposition of the Ag film onto the LiPON on the OHARA plate,
25 120 μm thick Li foil from Cyprus Foote Mineral Co. was pressed onto the Ag film to fabricate a thick protected Li anode. A Carver hydraulic press located in a dry room was used for the pressing operation. The applied pressure was around 800 kg/cm^2 , and duration of pressing was 10 minutes. The Li surface was polished with a Tyvec fabric just before pressing onto the Ag film. The Ag film reacted with the Li foil forming a
30 strong reaction bond.

Fig. 26 shows a discharge (potential-time) curve at discharge rate of 0.3 mA/cm^2 . The cell exhibited long discharge with a high average discharge voltage of 2.9 V. Discharge capacity delivered to the cut-off voltage of 2.5 V was more than 10

anode. The protected anode was fitted into an electrochemical cell by use of an o-ring such that the OHARA plate was exposed to the aqueous environment.

The electrolyte used in this Li/air cell with protected anode was comprised of 1 M LiOH. The volume of the electrolyte was approximately 0.2 ml. An air electrode
5 from commercial Zn/Air batteries was used as a cathode in our experimental Li/Air cell.

Fig. 27 shows discharge/charge potential-time curves at discharge/charge rate of 1.0 mA/cm². The duration of each discharge and charge was 3 minutes. Even though the air electrodes used in these experiments were designed for single
10 discharge, the cell delivered 10 cycles without significant increase in electrode polarization. This result demonstrates that a protected Li anode Li/air cell in accordance with the present invention can work reversibly.

Conclusion

Although the foregoing invention has been described in some detail for
15 purposes of clarity of understanding, it will be apparent that certain changes and modifications may be practiced within the scope of the appended claims. In particular, while the invention is primarily described with reference to a lithium metal anode, the anode may also be composed of any active metal, in particular, other alkali metals, such as sodium. It should be noted that there are many alternative ways of
20 implementing both the process and compositions of the present invention. Accordingly, the present embodiments are to be considered as illustrative and not restrictive, and the invention is not to be limited to the details given herein.

All references cited herein are incorporated by reference for all purposes.

11. The cell of claim 10, wherein the aqueous electrolyte is sea water.
12. The cell of claim 10, wherein the aqueous electrolyte comprises sea water and hydrogen peroxide.
13. The cell of claim 9, wherein the aqueous electrolyte comprises an acidic peroxide solution.
14. The cell of claim 9, wherein hydrogen peroxide dissolved in aqueous electrolyte flowing through the cell.
15. The cell of claim 2, wherein the cathode structure electronically conductive component is a porous catalytic support.
16. The cell of claim 15, wherein the porous catalytic electronically conductive support is reinforced.
17. The cell of claim 15, wherein the porous catalytic electronically conductive support comprises nickel.
18. The cell of claim 15, wherein the porous catalytic electronically conductive support comprises an inert material impregnated with a water reducing catalyst.
19. The cell of claim 15, wherein the porous catalytic electronically conductive support is treated with an ionomer.
20. The cell of claim 2, wherein the cell has an open cell voltage of at least 2 V.
21. The cell of claim 12, wherein the cell has a flat discharge potential of at least 3.5 V.
22. The cell of claim 14, further comprising a separator disposed between the protective membrane and the cathode structure.
23. The cell of claim 1, further comprising a PEM H_2/O_2 fuel cell to capture hydrogen released from the cathode structure in the battery cell redox reaction.
24. The cell of claim 1, wherein the cathode structure electrochemically active material comprises air.
25. The cell of claim 24, wherein the air comprises moisture.
26. The cell of claim 25, wherein the ionically conductive material comprises an aqueous constituent.
27. The cell of claim 26, wherein the ionically conductive material further comprises an ionomer.

46. The cell of claim 44, wherein the cathode structure electrochemically active material comprises air.
47. The cell of claim 44, wherein the cathode structure electrochemically active component comprises a metal hydride alloy.
48. The cell of any preceding claim, wherein the ionic conductivity of the protective membrane is at least 10^{-7} S/cm.
49. The cell of any preceding claim, wherein the ionic conductivity of the protective membrane is at least 10^{-5} S/cm.
50. The cell of any preceding claim, wherein the ionically conductive protective membrane comprises a composite, the composite comprising,
a first material component in contact with the anode that is ionically conductive and chemically compatible with the active metal of the anode, and
a second material component in contact with the first material component, the second material being substantially impervious, ionically conductive and chemically compatible with the first material component and the cathode structure.
51. The cell of claim 50, wherein the protective composite is a laminate.
52. The cell of claim 50, wherein the protective composite is graded.
53. The cell of claim 50, wherein the active metal of the negative electrode is lithium or a lithium alloy.
54. The cell of claim 50, wherein the first component comprises a material selected from the group consisting of active metal nitrides, active metal phosphides, and active metal halides, and active metal phosphorus oxynitride glass.
55. The cell of claim 50, wherein the first layer comprises a material selected from the group consisting of Li_3N , Li_3P and LiI , LiBr , LiCl , LiF , and LiPON .
56. The cell of claim 50, wherein the second component comprises a material selected from the group consisting of glassy or amorphous metal ion conductors, ceramic active metal ion conductors, and glass-ceramic active metal ion conductors.
57. The cell of claim 50, wherein the second component is an ion conductive glass-ceramic having the following composition:

Composition	mol %
P_2O_5	26-55%

GeO ₂ + TiO ₂	25-50%
in which GeO ₂	0--50%
TiO ₂	0--50%
ZrO ₂	0-10%
M ₂ O ₃	0 < 10%
Al ₂ O ₃	0-15%
Ga ₂ O ₃	0-15%
Li ₂ O	3-25%

and containing a predominant crystalline phase composed of $\text{Li}_{1+x}(\text{M}, \text{Al}, \text{Ga})_x(\text{Ge}_{1-y}\text{Ti}_y)_{2-x}(\text{PO}_4)_3$ where $X \leq 0.8$ and $0 \leq Y \leq 1.0$, and where M is an element selected from the group consisting of Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm and Yb and/or and $\text{Li}_{1+x+y}\text{Q}_x\text{Ti}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ where $0 < X \leq 0.4$ and $0 < Y \leq 0.6$, and where Q is Al or Ga.

67. A electrochemical cell structure, comprising:

an active metal anode having a first surface and a second surface;

a porous catalytic electronically conductive support;

an ionically conductive protective membrane on the first surface of the anode, the membrane comprising,

one or more materials configured to provide a first surface chemically compatible with the active metal of the anode, and a second surface substantially impervious to and chemically compatible with the catalytic electronically conductive support, and aqueous environments.

68. A method of making an electrochemical cell structure, comprising:

assembling an active metal anode and a cathode structure comprising an electronically conductive component;

wherein a protective membrane is disposed between the active metal anode and the cathode structure, the membrane being ionically conductive and chemically compatible with an active metal on a first side, and substantially impervious, ionically conductive and chemically compatible the cathode structure on the other side;

and wherein an active metal material is applied to the first side of the protective membrane to form the active metal anode.

69. The method of claim 68, wherein the electronically conductive component of the cathode structure is a porous nickel sheet.

1/29

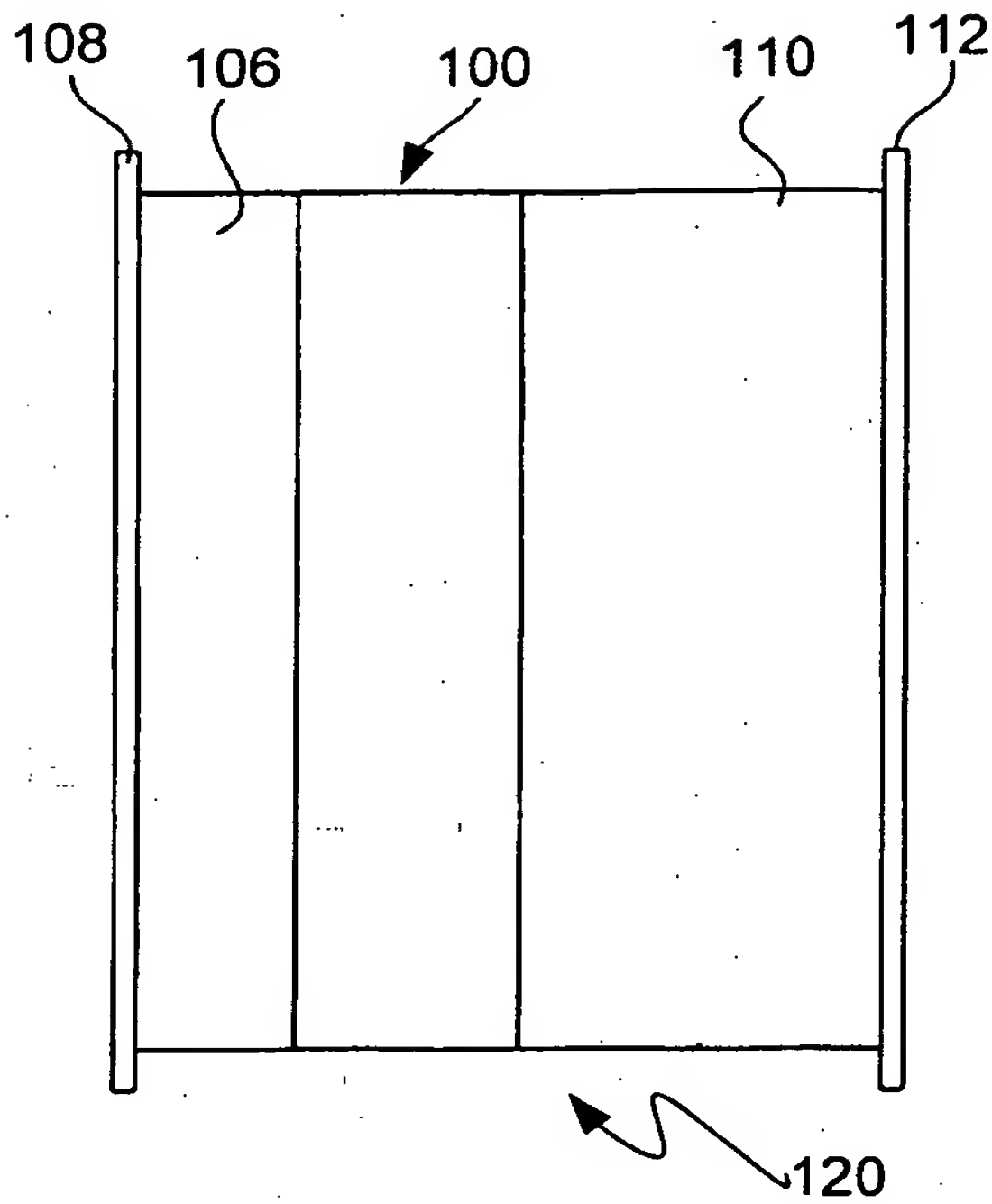


FIG. 1

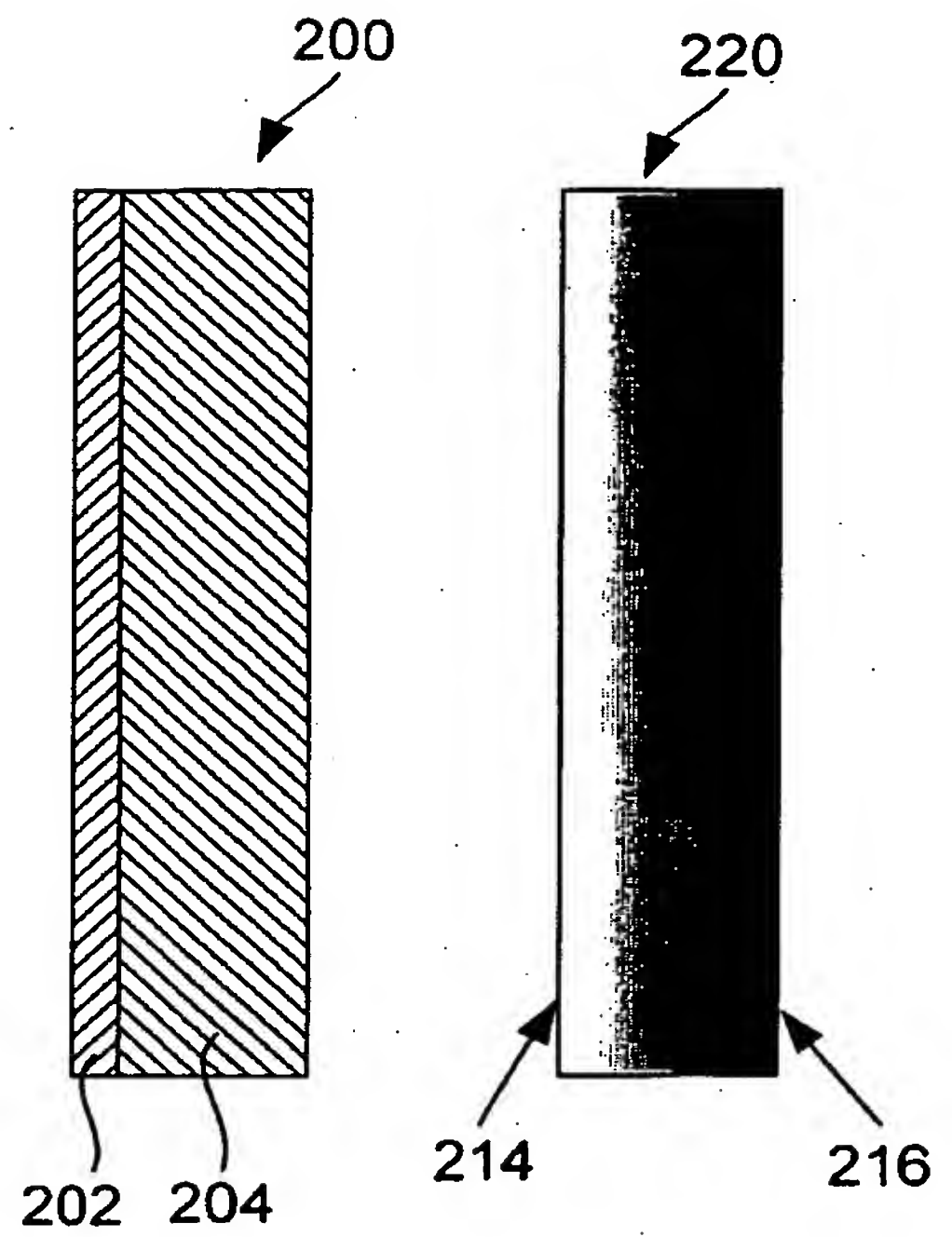


FIG. 2A FIG. 2B

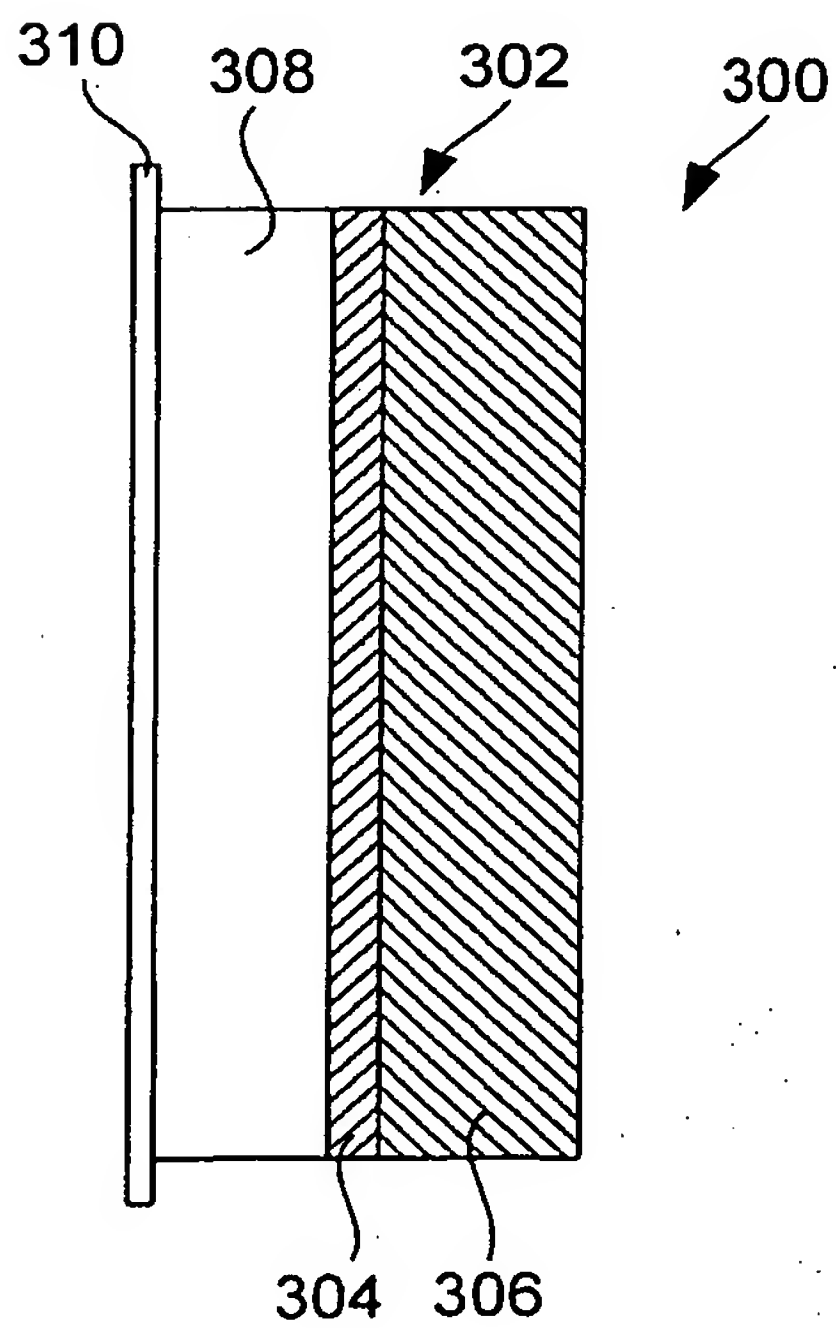


FIG. 3A

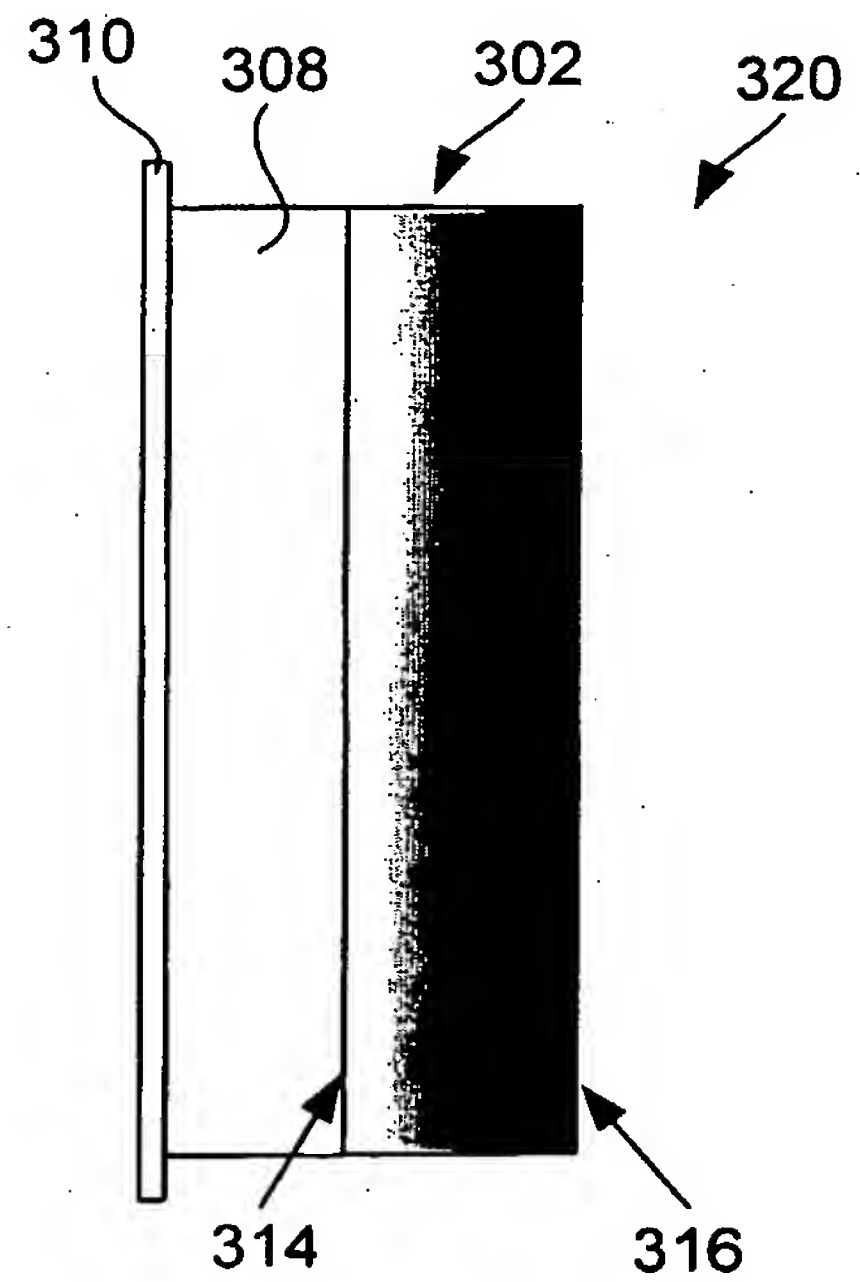


FIG. 3B

Plasma spray, Physical Vapor Deposition, etc.

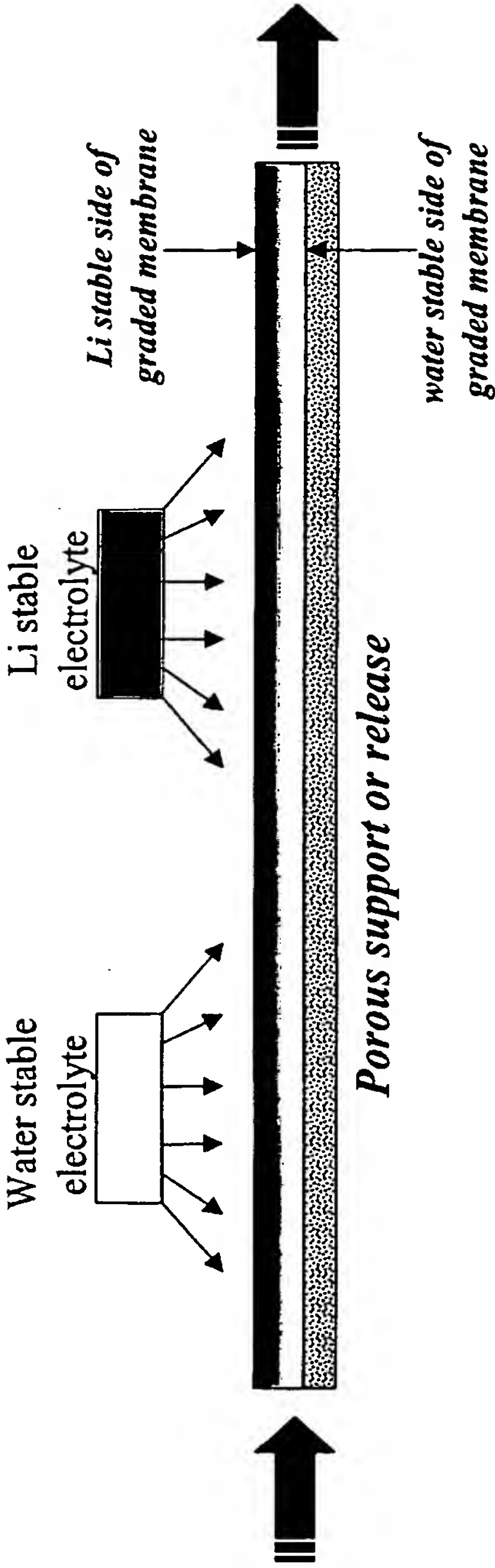
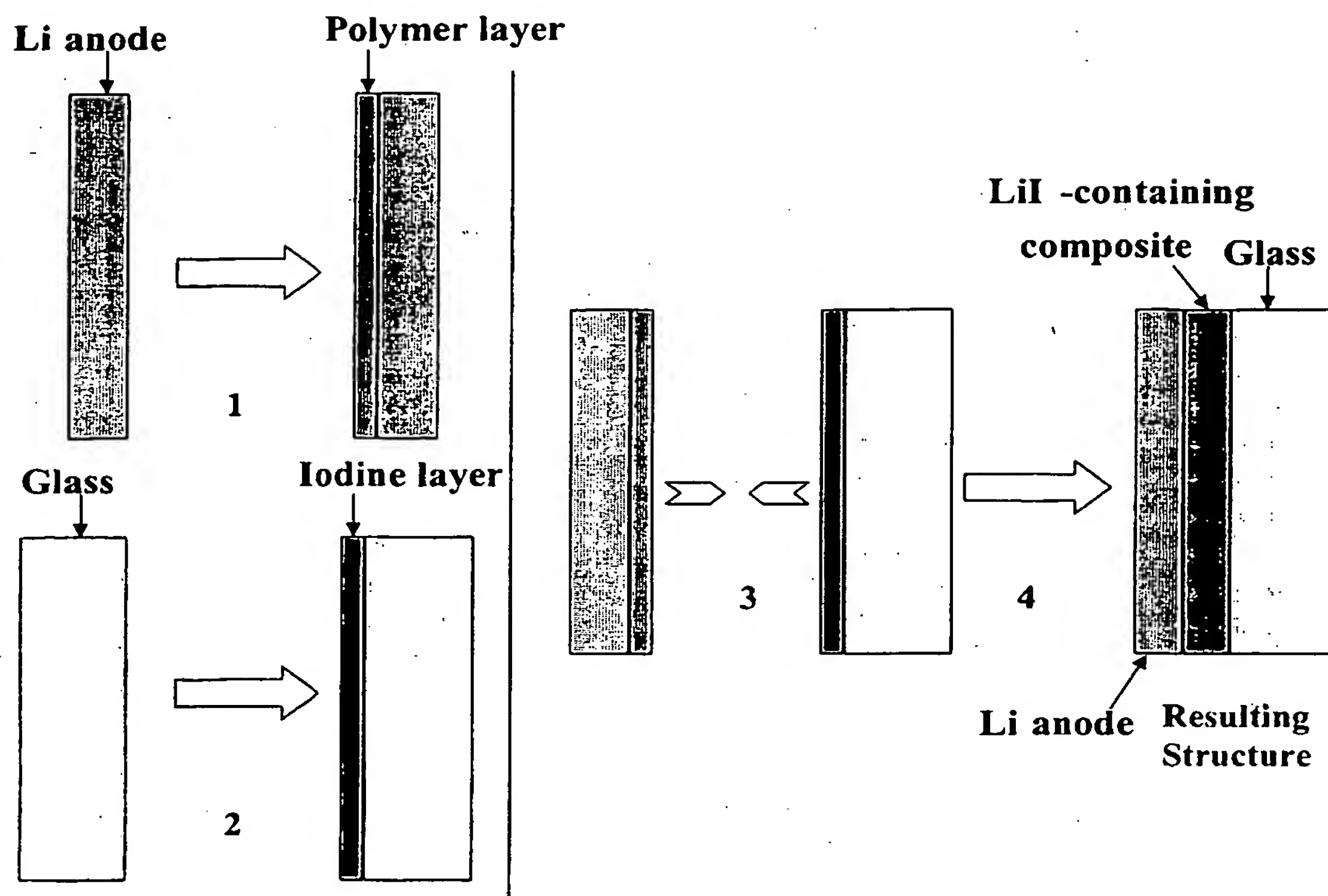
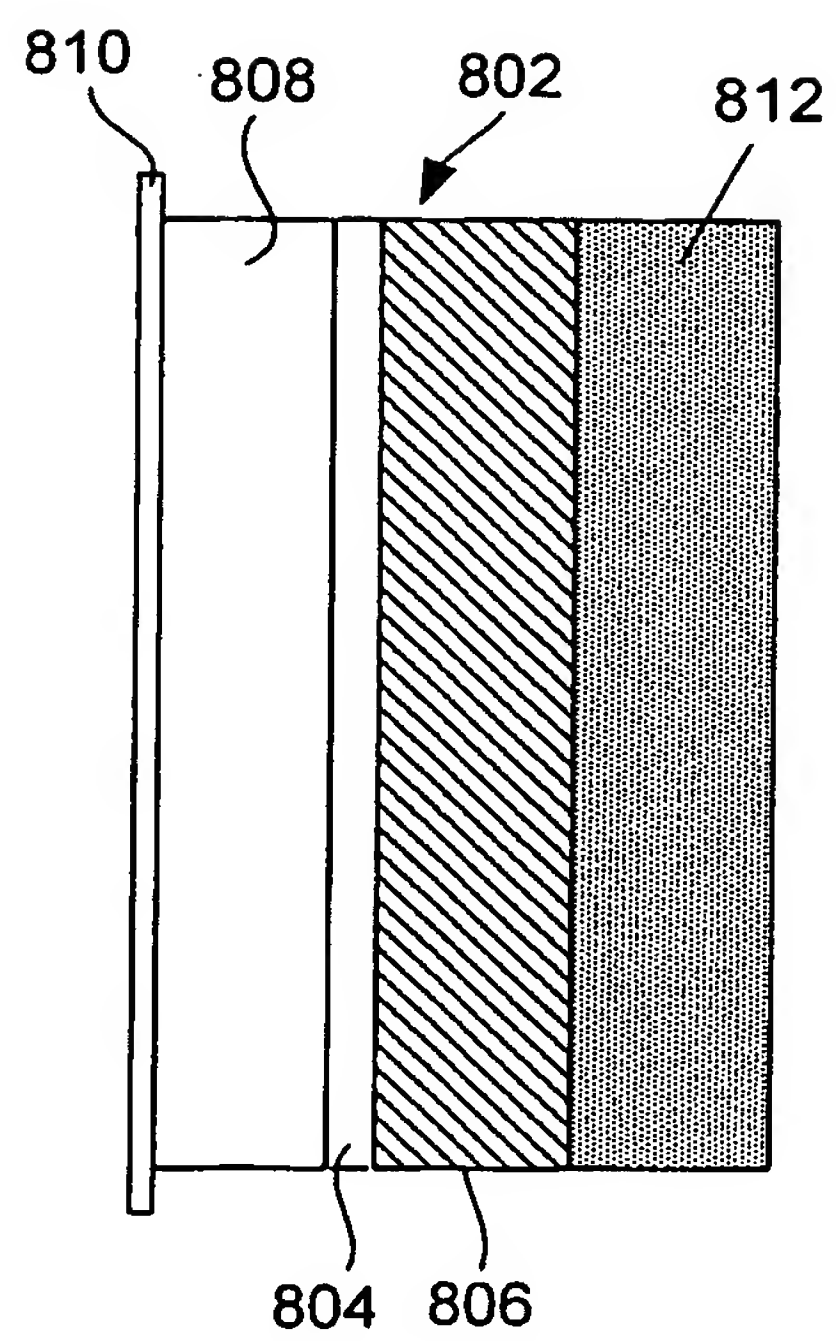


FIG. 5

5/29

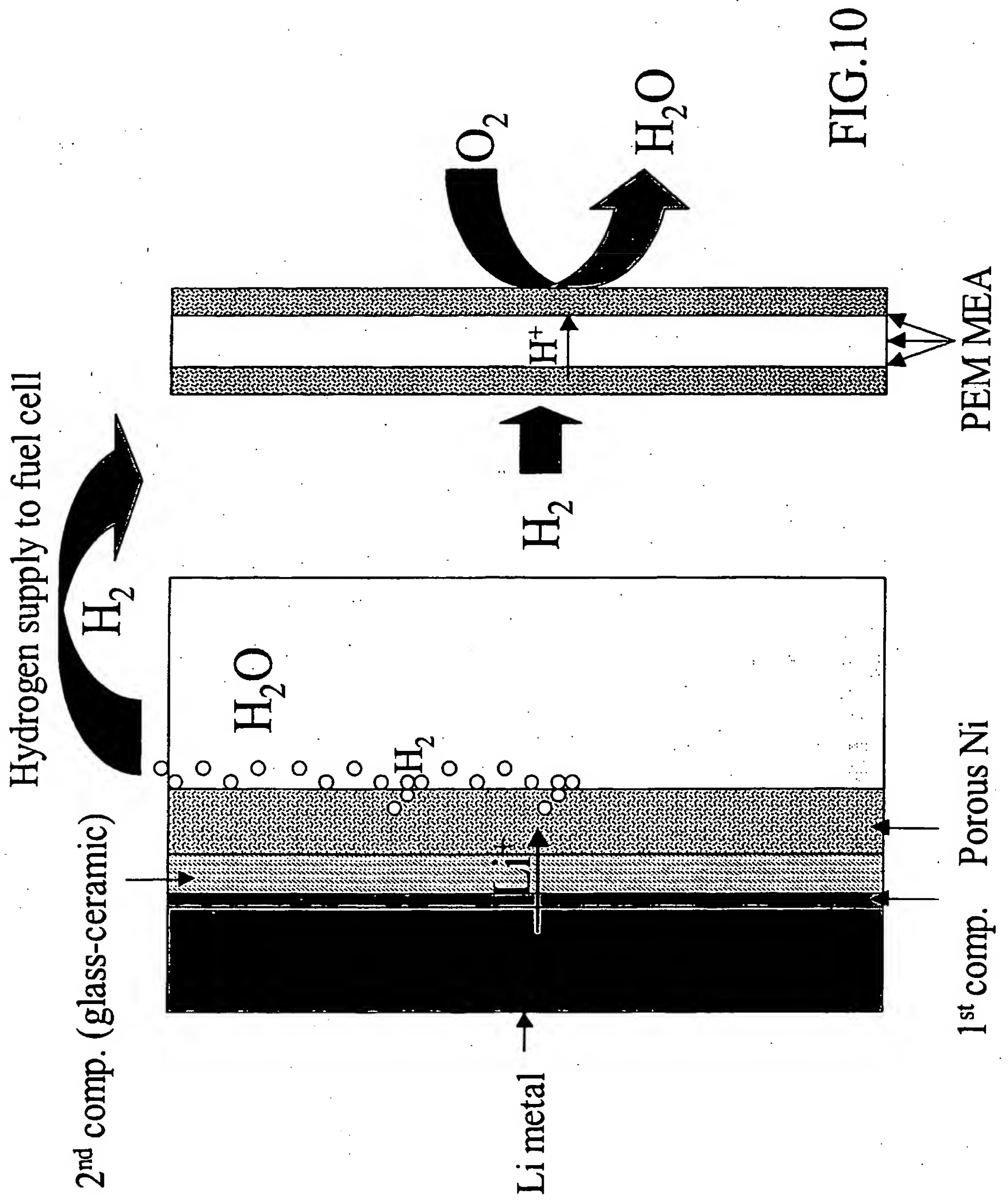
**FIG. 6B**

7/29

**FIG. 8**

9/29

Li/ water Battery and Hydrogen Generator for Fuel Cell



11/29

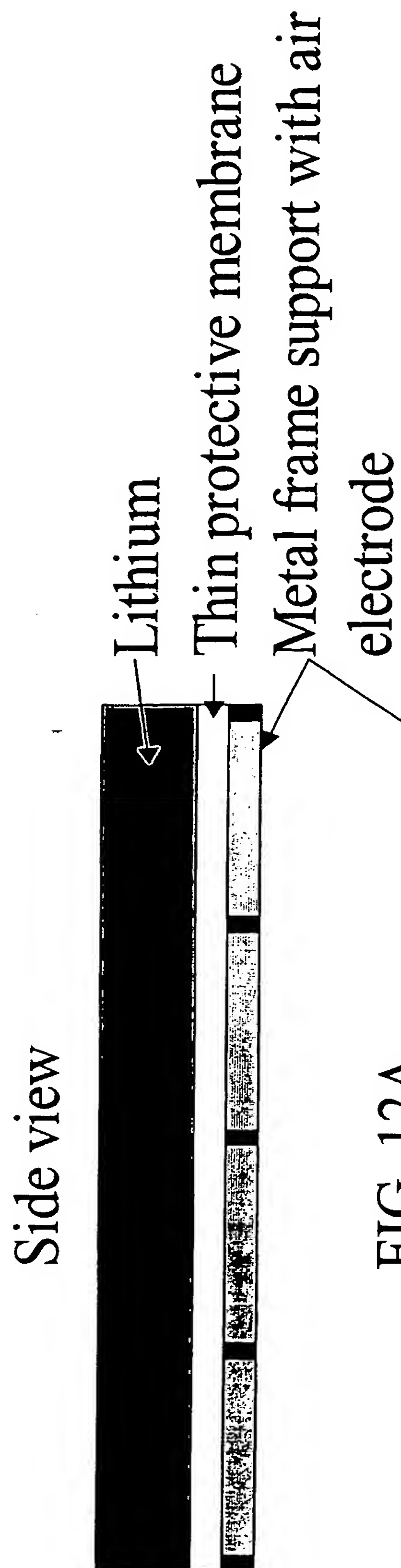
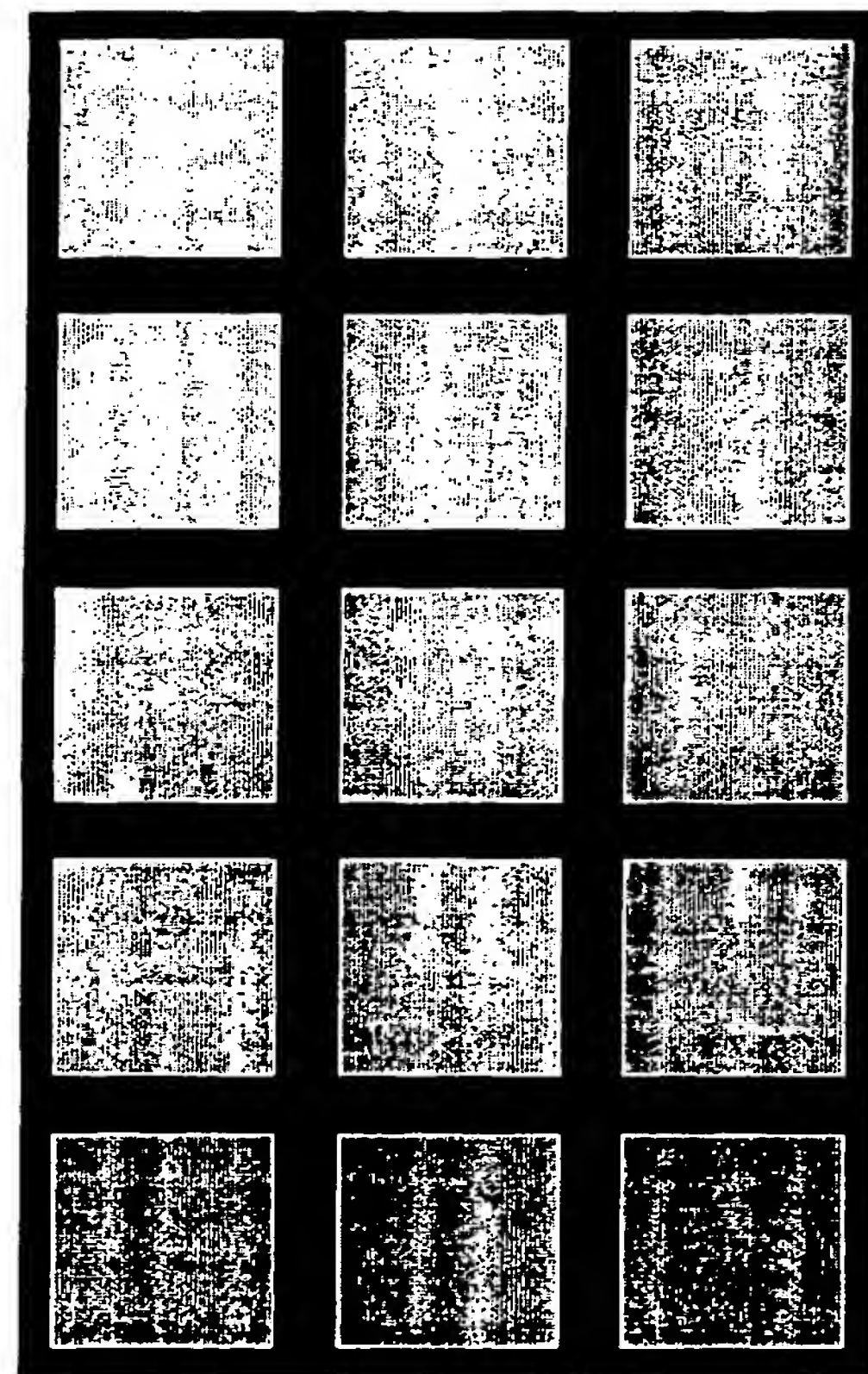
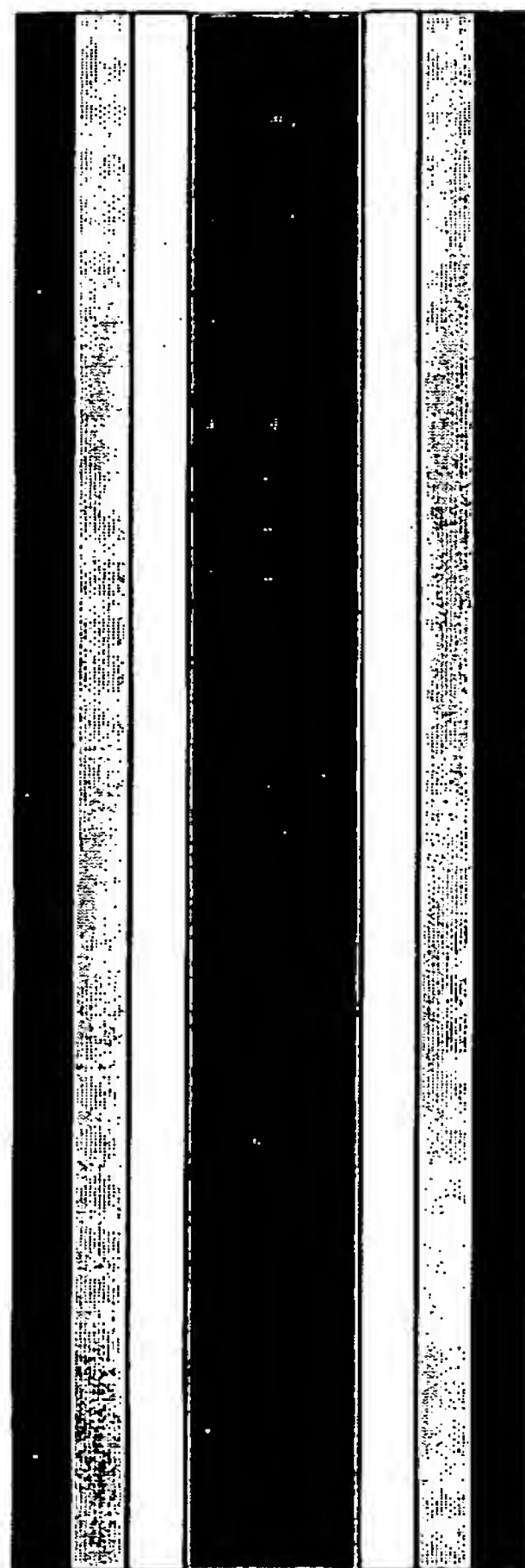


FIG. 12A



Bottom view
FIG. 12B

Side view



Li/water or Li/air bilayer structure

FIG. 12E

Tubular Li-water or Li-air cell

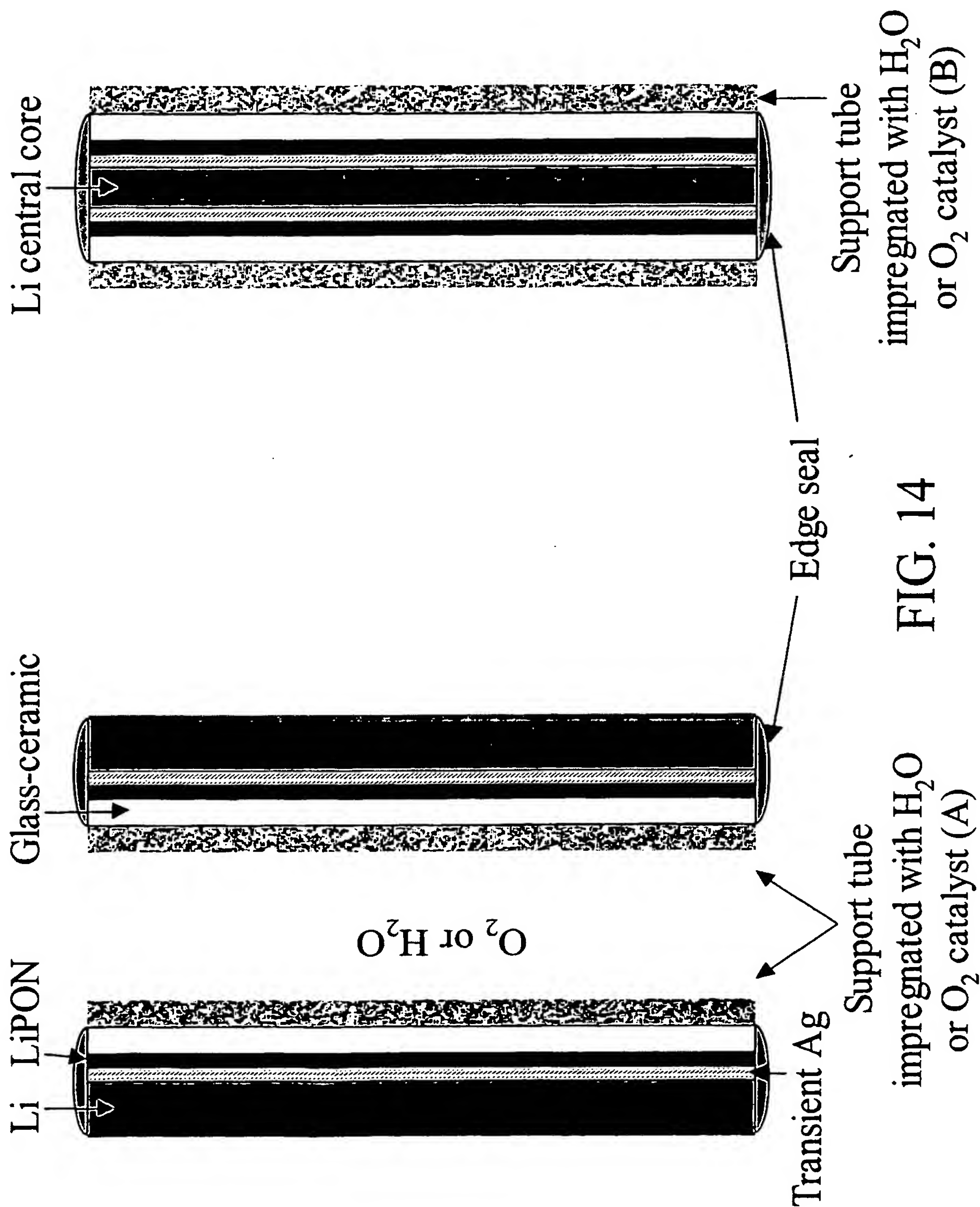


FIG. 14

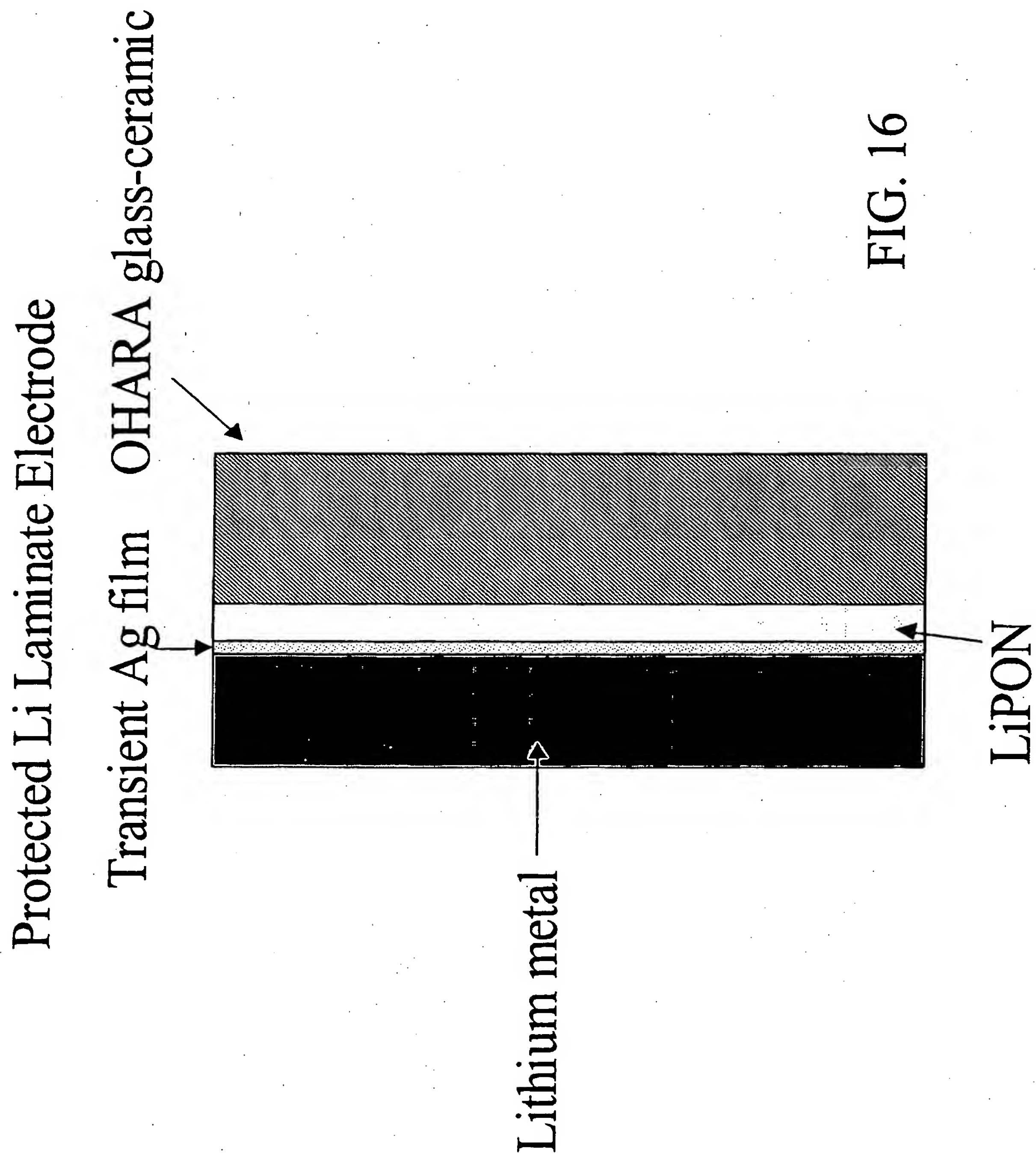


FIG. 16

Potential – time Curve for H₂ Evolution at Pt Cathode in the Cell with Li Protected Anode

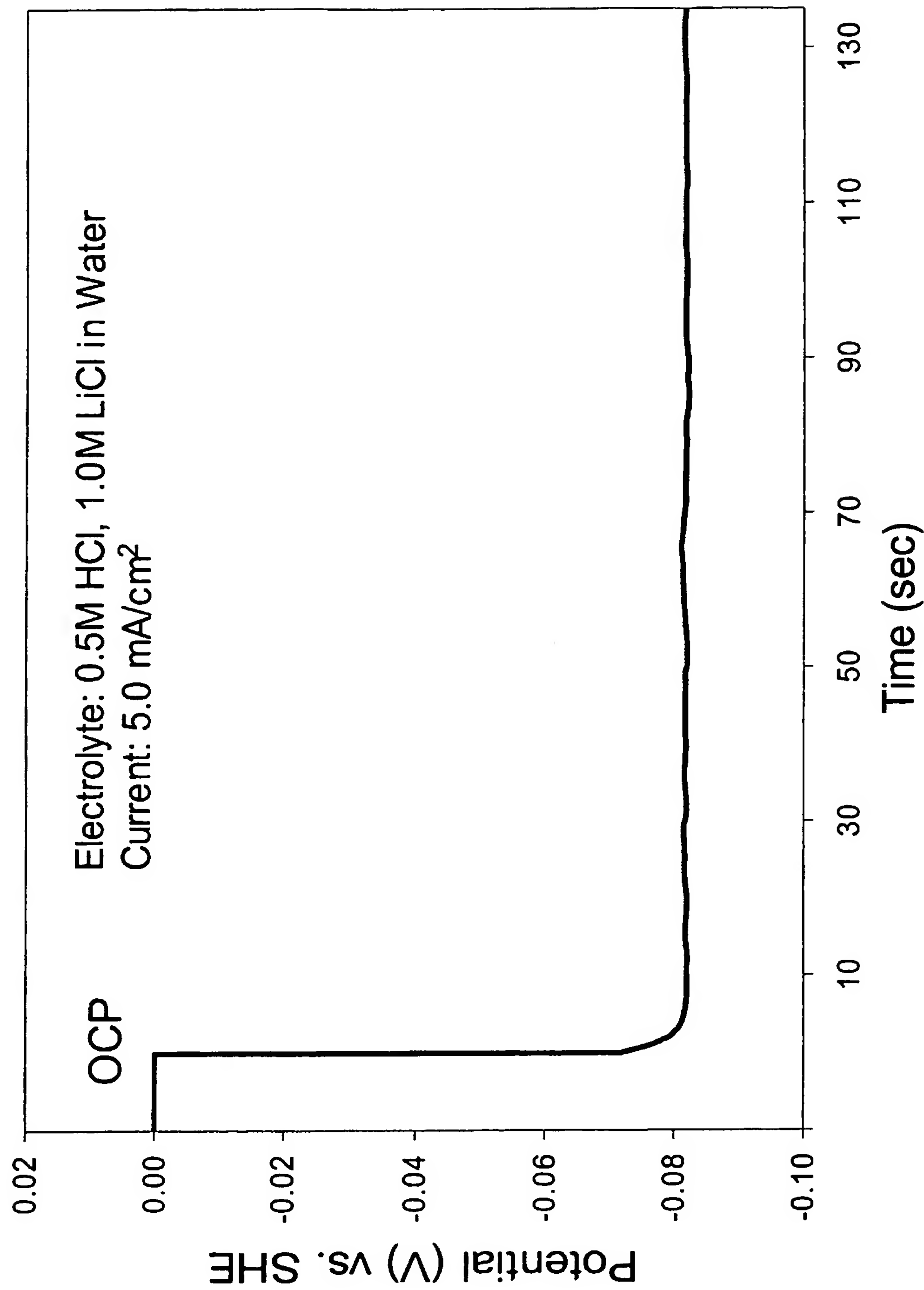


FIG. 18

21/29

Cycling of Protected Li Anode in Aqueous Electrolyte

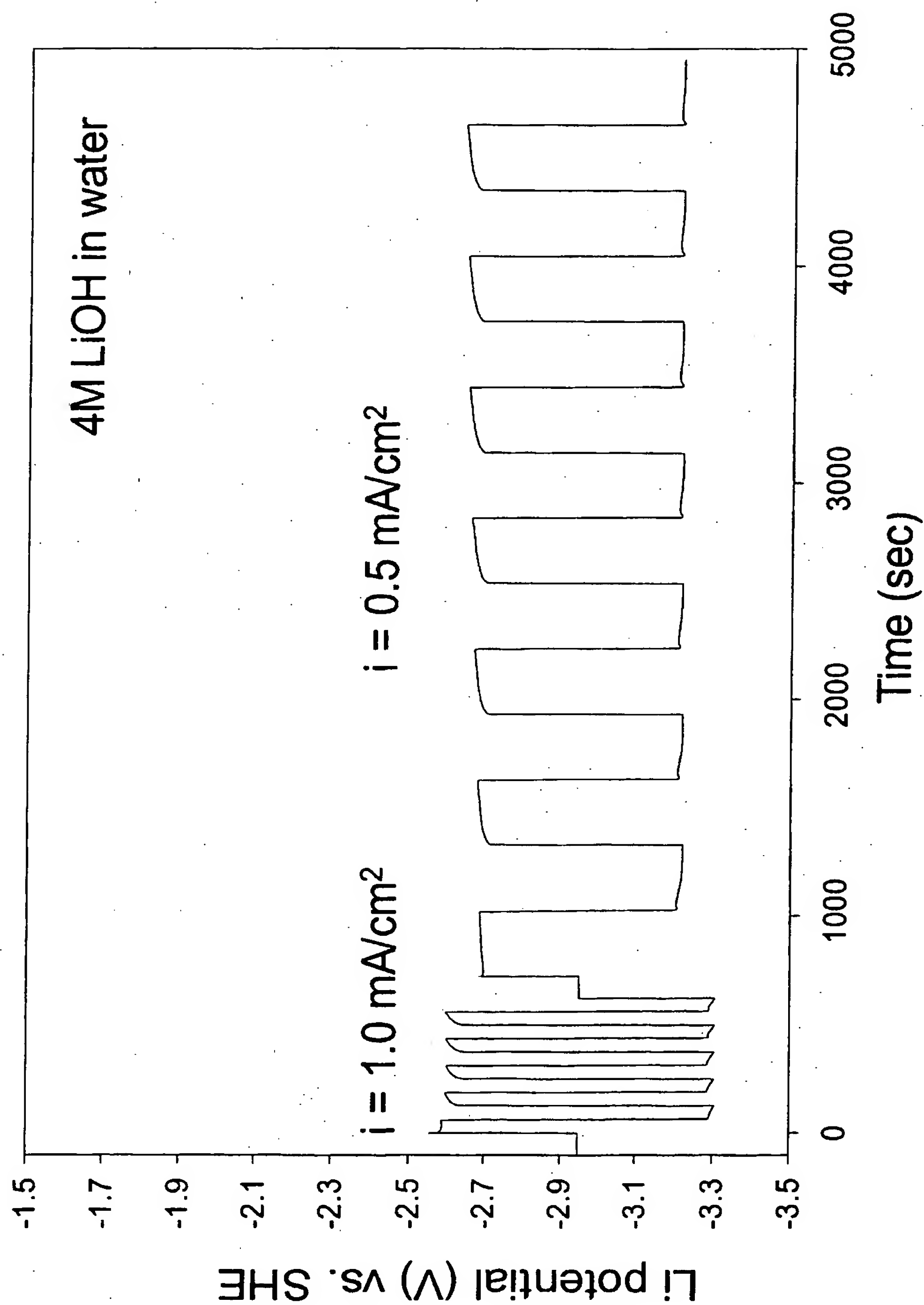


FIG. 20

Potential-time Curve for Anodic Dissolution of Protected Li Electrode in Seawater

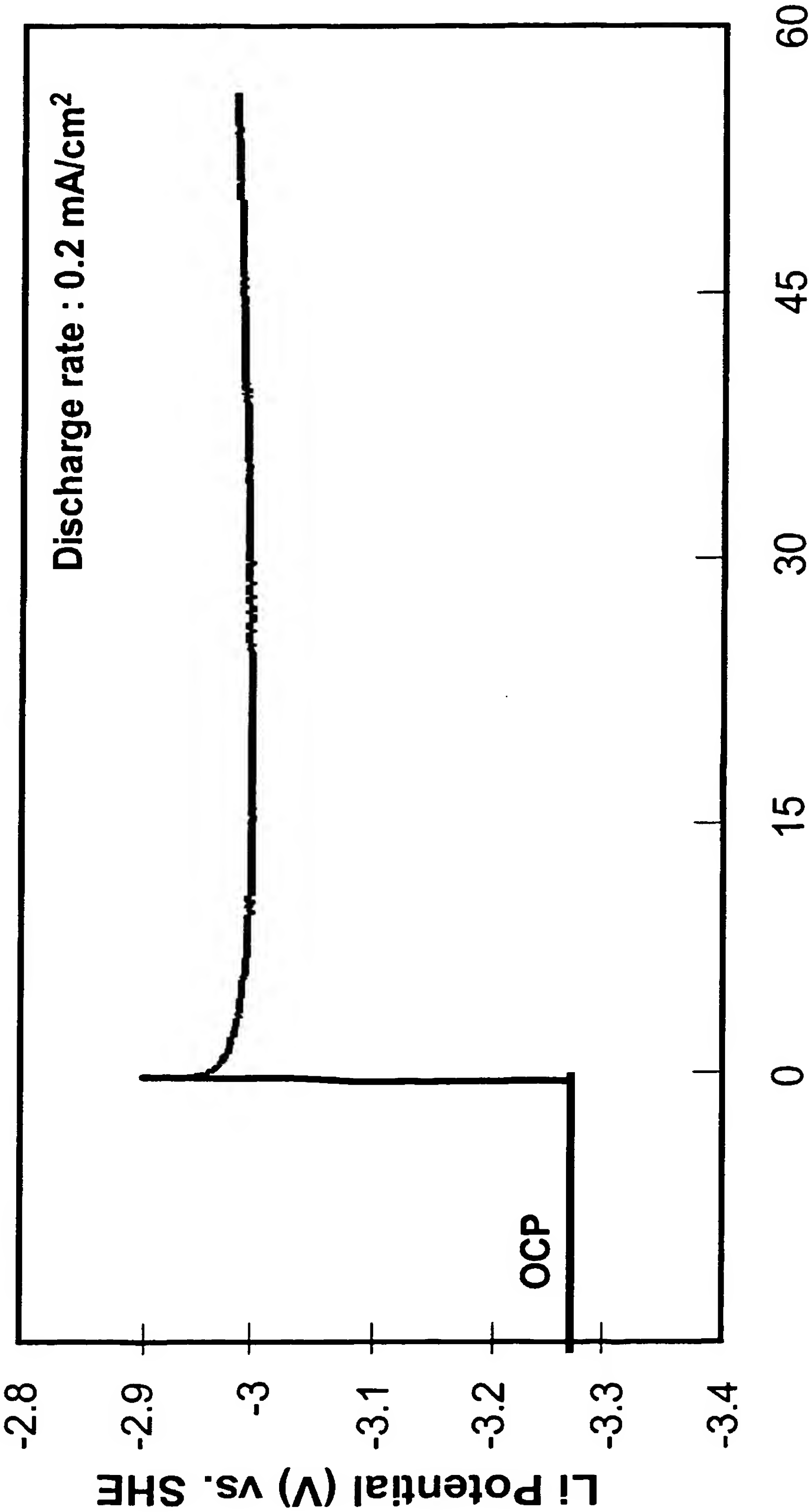


FIG. 22A

Discharge of Protected Li Anode in Seawater

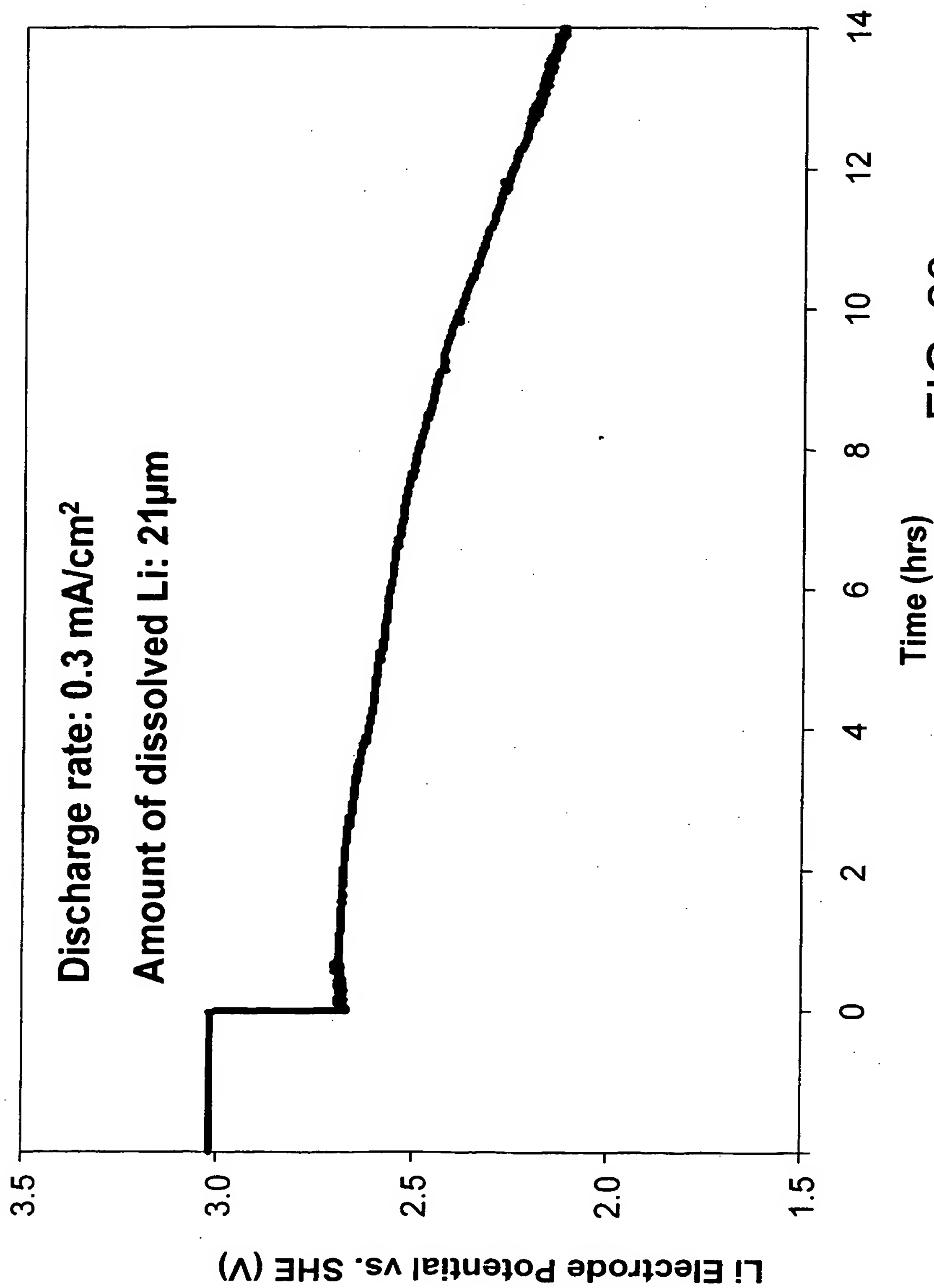


FIG. 23

27/29

Discharge of Li/Air Cell with Protected Li Electrode and Neutral Electrolyte

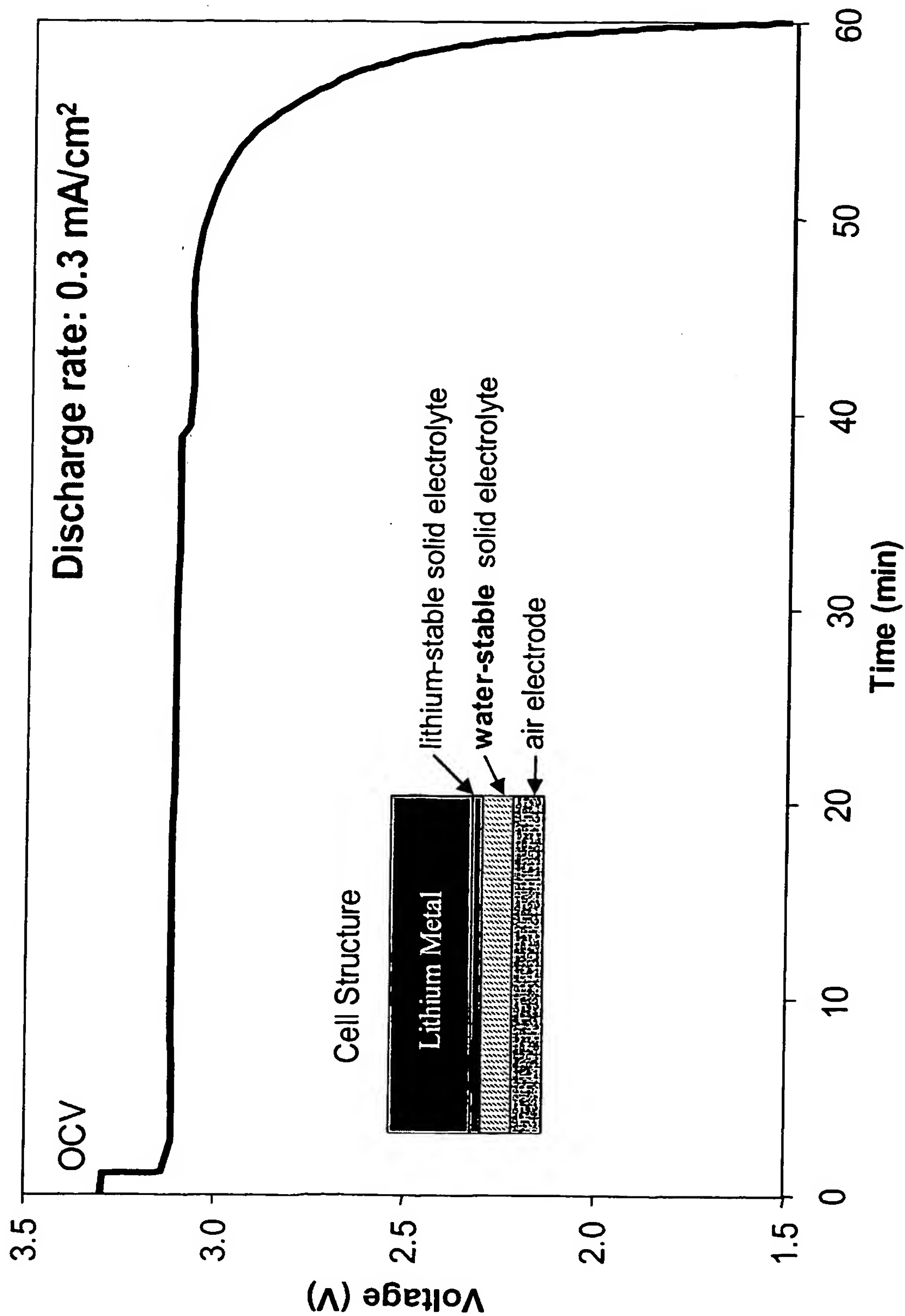


FIG. 25

29/29

Cycling of Li/Air cell with Protected Li Electrode

Charge/Discharge Rate: 1.0 mA/cm²

Electrolyte: 1 M LiOH

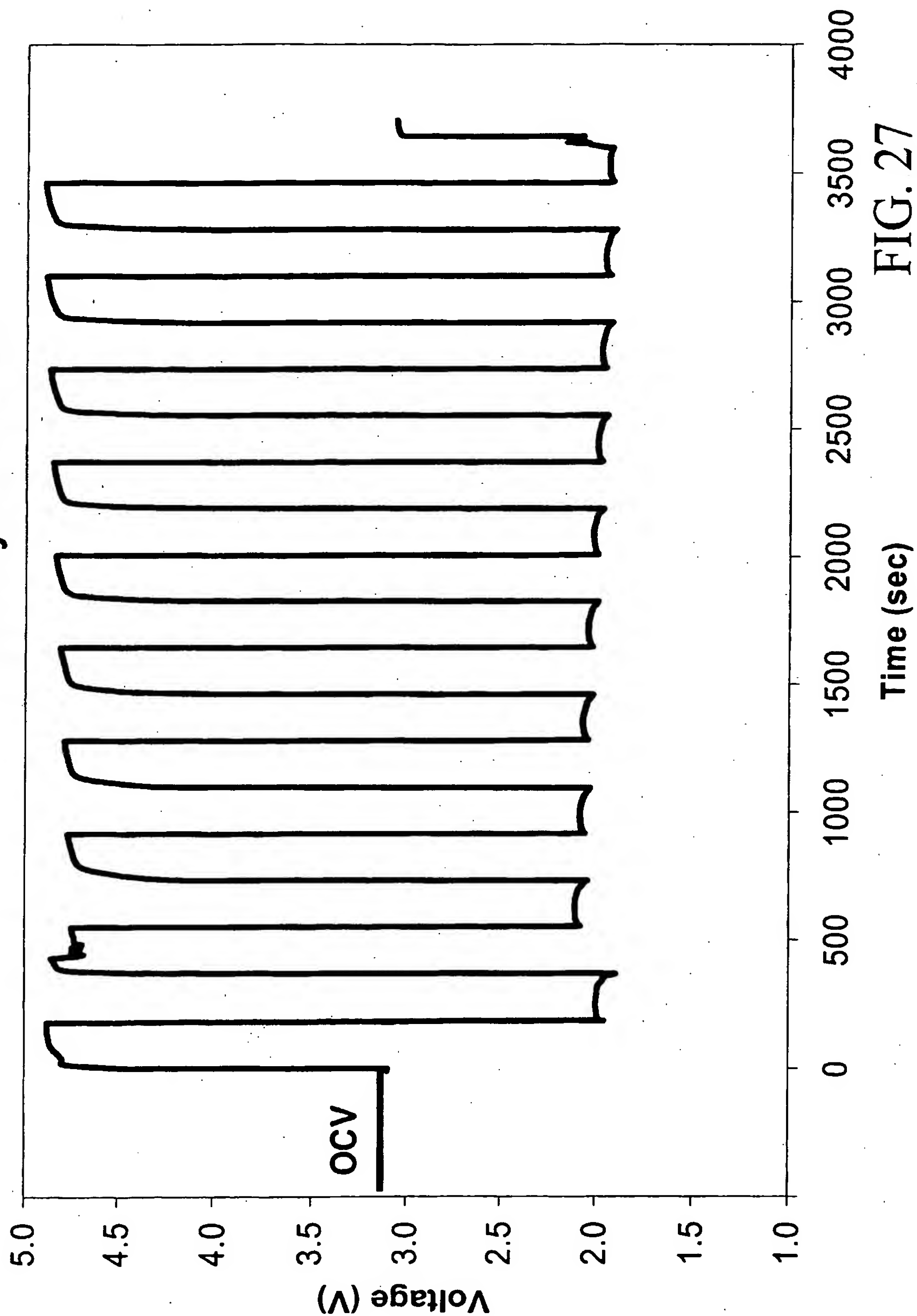


FIG. 27

THIS PAGE BLANK (USPTO)